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In situ reflection absorption spectroscopic techniques for the study of electrogenerated species

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Case Western Reserve University, 1993
IN SITU REFLECTION ABSORPTION SPECTROSCOPIC TECHNIQUES FOR THE STUDY OF ELECTROGENERATED SPECIES

by

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Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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GRADUATE STUDIES

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*We also certify that written approval has been obtained for any proprietary material contained therein.
IN SITU REFLECTION ABSORPTION
SPECTROSCOPIC TECHNIQUES
FOR THE STUDY OF ELECTROGENERATED SPECIES

Abstract

by

MING ZHAO

This dissertation focuses on the development of in situ reflection absorption spectroscopic techniques and their applications. In particular, a new technique is described in which the surface of a rotating disk electrode (RDE) is used as a mirror to reflect light in the UV-visible range at a near normal incidence angle to probe quantitatively absorbing species in the diffusion boundary layer under well-defined hydrodynamic conditions. The analysis of static measurements involving the oxidation of Fe(CN)$_6^{4-}$ as a model system was found to be in good agreement with the theory based on hydrodynamics and optics. The time evolution of the integrated profile of Fe(CN)$_6^{3-}$ species generated at the surface of the RDE by a potential step was also monitored using the same method yielding transient curves in harmony with those predicted by the theory without introducing any adjustable parameters.

Further extensions of this experimental arrangement to include the application of a sinusoidal voltage of small amplitude to the RDE to modulate the absorptivity of the solution were also examined. All theoretical predictions were verified experimentally using the oxidation of Fe(CN)$_6^{4-}$ as a probe reaction.
An instrumental arrangement is described for the acquisition of in situ near normal incidence reflection absorption magnetic circular dichroism (MCD) spectra of the electrode surface. The potential modulated MCD of the basal plane of highly oriented pyrolytic graphite in acid electrolytes was examined. The magnitude of the MCD signal as a function of the applied potential increased with the strength of the external magnetic field. MCD spectra have been also recorded of solution-phase cobalt 4,4',4",4"" sulphonated phthalocyanine in the Co(II) and Co(III) forms. These highly detailed in situ spectra were found to be in agreement with those reported in the literature.

In situ Fourier Transform Infrared Reflection Absorption Spectroscopy (FTIRRAS) was used to elucidate mechanistic pathways associated with the reduction of nitrate on Au mediated by Cd-UPD. On the basis of these measurements it was concluded that the electrocatalytic process yields quantitatively solution-phase nitrite as the only detectable product for \([\text{H}^+] < [\text{NO}_3^-]\). The spectral properties of CO adsorbed on nickel electrodes in alkaline solution have also been examined using in situ FTIRRAS. The results show that the voltammetric peak in the first linear scan in the positive direction for Ni(poly)/CO(ads) surfaces is associated with the electrochemical oxidation of bridge-bonded CO to generate solution-phase carbonate as the only detectable product. The stretching frequency of CO shifted toward lower wavenumbers as the coverage of CO was reduced by electrooxidative stripping.
To my parents, my wife Songqi and our daughter Jenny
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CHAPTER I

INTRODUCTION

An unambiguous identification of intermediates and products of heterogeneous electron transfer reactions at electrode/electrolyte interfaces is crucial to the further understanding of electrochemical kinetics. Considerable progress has been made over the past few decades toward the development and implementation of spectroscopic techniques for the \textit{in situ} electronic, vibrational and structural characterization of adsorbed and/or solution-phase electrogernated species.\textsuperscript{1-3} These advances have opened new prospects for the elucidation of reaction mechanisms at these interfaces, which are expected to have a profound impact in areas of crucial fundamental and technological importance particularly electrocatalysis, energy conversion and energy storage.

The work presented in this dissertation may be divided into three distinct areas:

- Development of new strategies for the quantitative detection of optically absorbing electrogernated species under well defined conditions of hydrodynamic flow, by coupling near normal incidence UV-visible reflection absorption spectroscopy\textsuperscript{4,5} to a rotating disk electrode (RDE)\textsuperscript{6-9}. 

1
- Implementation of reflection absorption magnetic circular dichroism (MCD)\textsuperscript{10-14} for the detection and identification of solution phase electrogenerated species.

- Application of reflection absorption Fourier transform reflection absorption spectroscopy (FTIR-RAS)\textsuperscript{15,16} to the study of adsorbed and solution phase electrogenerated species.

This dissertation has been organized in eight chapters, excluding this brief Introduction. Each chapter has been written in the form of a formal paper and in most instances is a verbatim copy of a published manuscript.

Chapter II introduces various experimental and theoretical aspects of near normal incidence reflection absorption spectroscopy as a probe of the optical properties of species present in the diffusion boundary layer generated by a RDE under quasi-steady state electrochemical conditions. This as well as all other experiments involving this coupled spectroscopic/hydrodynamic method employed the oxidation of [Fe(CN)\textsubscript{6}]\textsuperscript{4-} to the optically absorbing [Fe(CN)\textsubscript{6}]\textsuperscript{3-} as the product as a model system. Applications of this technique to monitor quantitatively transient convective diffusion to a RDE are given in Chapter III. A complete theoretical and experimental treatment of potential modulated near normal incidence reflection absorption spectroscopy at a RDE is given in Chapters IV and V, respectively. Various experimental and
theoretical aspects of in situ reflection MCD are addressed in Chapters VI and VII including the description of a new arrangement to measure the MCD spectra of solution phase electrogenerated species using cobalt tetrasulfonated phthalocyanine (CoTsPc) as a model system. The final two chapters describe applications of FTIRRAS to the study of systems of interest to electrocatalysis including the reduction of nitrate to nitrite mediated by underpotential deposited cadmium on a gold electrode (Chapter VIII) and the oxidation of irreversibly adsorbed carbon monoxide on a nickel electrode in alkaline solutions (Chapter IX).

REFERENCES


PART ONE

IN SITU UV-VISIBLE REFLECTION ABSORPTION SPECTROSCOPY UNDER FORCED CONVECTION
CHAPTER II

UV-VISIBLE REFLECTION ABSORPTION SPECTROSCOPY IN
THE PRESENCE OF CONVECTIVE FLOW*

II-1. INTRODUCTION

The advent of a variety of in situ spectroscopic techniques has opened new prospects for the further understanding of heterogeneous electron transfer and other interfacial processes.¹ In their present stage of development, however, most of these methods lack sufficient time resolution to enable the detection and identification of short-lived reaction intermediates. Attempts have been made over the past fifteen years to overcome some of these limitations by using forced convection.²⁻⁴ With the exception of the rotating disk electrode/optically transparent (insulating) ring arrangement introduced by Debrodt and Heusler³ and later rigorously analyzed by Dorr and Grabner,⁴ the hydrodynamic characteristics of the fluid flow have not been well defined.

This chapter describes a novel strategy in which in situ UV-visible reflection absorption spectroscopy has been coupled to a rotating disk electrode. As will be shown, this approach makes it possible to monitor the concentration of (sufficiently) absorbing electroactive species present

* This chapter has been published:
in the diffusion boundary layer. Furthermore, experiments involving the oxidation of Fe(CN)$_6^{4-}$ to Fe(CN)$_6^{3-}$ have indicated that the technique can indeed yield quantitative data.

II-2. THEORETICAL CONSIDERATIONS

A. Hydrodynamics

Within the framework of approximations discussed elsewhere$^5$, the steady state concentration profile of a species in the presence of the convective flow generated by a rotating disk electrode is given by

$$
\frac{[c(\zeta) - c^o]}{[c^s - c^o]} = 1 - \left( \frac{1}{0.8934} \right) \int_0^{\zeta} \exp \left( -\zeta^3 \right) d\zeta
$$

(II-1)

where $c(\zeta)$ is the (local) concentration of the species, the superscripts $o$ and $s$ refer to the magnitudes of $c$ in the bulk of the solution and at the electrode surface, respectively. The variable $\zeta = y/\delta$ in Eq. II-1 is a dimensionless coordinate normal to the electrode surface, where $y$ is the actual distance from the surface (in cm) and $\delta = 1.805D^{1/3}\nu^{1/6}\Omega^{-1/2}$, the thickness of the diffusion boundary layer, in which $D$ is the diffusion coefficient of the species (in cm$^2$/s), $\nu$ is the kinematic viscosity of the solution (in cm$^2$/s) and $\Omega$ the rotation rate of the disk in radians/s.

Consider a cell such as that shown in Figure. II-1, in which the axis of rotation is normal to the bottom of the cell placed at a distance $L$
Figure II-1. Schematic diagram of the experimental arrangement for reflection absorption UV-visible spectroscopy on a rotating disk electrode at near normal incidence angle. In and out refer to the incoming and outgoing beams, respectively.
(ζ = L/δ) from the electrode surface (ζ = 0). The total amount of the species (per unit cross sectional area) along the ζ axis can be obtained by rearranging and integrating Eq. II-1 between the appropriate limits to yield

$$\int_0^{L/δ} c\,dζ = c^0 L/δ + \left[c^s - c^0 \right] \left[1 - \left( \frac{1}{0.8934} \right) \right] \int_0^ζ \exp(-ζ^3) \,dζ$$  \hspace{1cm} (II-2)

In practice, L is on the order of centimeters and therefore three orders of magnitude larger than δ, which is on the order of tens of microns. The integral on the right hand side of Eq. II-1 is rapidly convergent reaching a limiting value for ζ of about 2, and thus much smaller than L/δ. Therefore, and to a good degree of approximation, one can replace the upper integration limit by infinity and thus obtain a universal constant B, defined as

$$B = \int_0^∞ \left[1 - \left( \frac{1}{0.8934} \right) \int_0^ζ \exp(-ζ^3) \,dζ \right] \,dζ$$  \hspace{1cm} (II-3)

Evaluation of this constant by a simple numerical method yielded a value of 0.5055.

Based on simple algebraic manipulations, Eq. II-2 can be rewritten to read

$$\int_0^L c\,dy = c^0 L + \left[c^s - c^0 \right] δB$$  \hspace{1cm} (II-4)

This implies that in the case of a very fast heterogeneous electron transfer reaction, so that c^s is prescribed solely by the applied potential, the integrated profile at a constant potential is a linear function of the
thickness of the diffusion boundary layer, which in turn is proportional to $\Omega^{-1/2}$. This treatment implicitly assumes that despite the passage of current the bulk composition of the solution remains unaltered over the full duration of the experiments. Such conditions can be approximately fulfilled provided the current is small, the volume of solution large and the measurement time short.

B. Optics

According to Lambert-Beer's law, the absorbance of a sample is directly proportional to the concentration of the absorbing species. Hence, along the axis of rotation, $y$

$$\frac{dI}{I} = k \varepsilon c \, dy$$  \hspace{1cm} (II-5)

where $I$ is the intensity of the light, $k = 2.303$, and $\varepsilon$ the extinction coefficient of the electroactive species. Notice that the sign of one of the terms in Eq. II-5 has been reversed to account for the fact that the incoming light is attenuated in the direction of decreasing $y$ values to conform to the orientation of the axis defined for the hydrodynamics. Hence, for the incoming beam denoted as (in)

$$\int_{I_L^{(in)}}^{I_0^{(in)}} \frac{dI}{I} = k \varepsilon \int_{L}^{0} c \, dy$$  \hspace{1cm} (II-6)

where $I_L^{(in)}$ is the intensity of the beam entering the cell (at $y = L$) and $I_0^{(in)}$ that of the beam impinging of the electrode surface (at $y = 0$) after traversing the whole solution. Therefore, using Eq. II-4 the total
absorbance of the incoming beam can be obtained by integrating Eq. II-6 to yield

$$\ln(I_L(\text{in})/I_0(\text{in})) = k \varepsilon (c^0L + [c^S - c^0] \delta B)$$ \hspace{1cm} (II-7)

In direct analogy with the previous analysis, the absorbance of the outgoing (out) or reflected beam may be shown to be given by

$$\ln(I_0(\text{out})/I_L(\text{out})) = k \varepsilon (c^0L + [c^S - c^0] \delta B)$$ \hspace{1cm} (II-8)

From an optical viewpoint, metals such as gold are not perfect reflectors in the UV-visible spectral range; hence, the intensity of the light following reflection is, in general, smaller than that of the original beam just before reaching the electrode surface. Also to be considered is the fact that the reflectivity is also a function of the applied potential (\textit{vide infra}). Therefore, the total absorbance \( A \), as defined in the conventional sense, can be written as

$$A(E) = \log[I_L(\text{in})/I_L(\text{out})] = 2\varepsilon(c^0L + [c^S - c^0] \delta B) - \log \kappa(E)$$ \hspace{1cm} (II-9)

where \( \kappa(E) = I_0(\text{out})/I_0(\text{in}) \) represents the reflectivity loss at the specified potential. The absorbance in Eq. II-9 has been written as \( A(E) \) to stress the fact that \( c^S \) and therefore \( I_L(\text{out}) \) (although not explicitly labeled) are potential dependent. Eq. II-9 is a general expression that applies for an electrode polarized at any arbitrary potential \( E \). For example, if no electrochemical reaction takes place for \( E = E_O \), the concentration profile will be constant throughout the cell. Hence \( c^S = c^0 \) and Eq. II-9 reduces to

$$A(E_O) = \log[I_L(\text{in})/I_L(\text{out})] = 2\varepsilon c^0L - \log \kappa(E_O)$$ \hspace{1cm} (II-10)

For a simple redox process ( \( R \rightarrow O + ne^- \) ) in which both \( R \) and \( O \)
may be absorbing light, an expression for the total absorbance at a specific wavelength and potential can be obtained by adding the contributions arising from both species. Hence, from Eq. II-9

\[ A(E) = 2\varepsilon_O (c_O^0L + [c_O^S - c_O^0]\delta_O B) \]

\[ - 2\varepsilon_R (c_R^0L + [c_R^S - c_R^0]\delta_R B) \log \tau(E) \]  \hspace{1cm} (II-11)

where the subscripts O and R refer to the oxidized and reduced species.

C. Potential Difference UV-Visible Reflection Absorption Spectroscopy under Forced Convection

Consider a situation in which the absorbance for a system consisting of the reduced and oxidized forms of the redox couple introduced above is measured at two arbitrary potentials \( E_1 \) and \( E_2 \). Based on the arguments put forward earlier, the difference in the absorbance at the two potentials will be given by

\[ A(E_1) - A(E_2) = \log[I_L(\text{out},E_2)/I_L(\text{out},E_1)] = 2\varepsilon_O \delta_O B[c_O^S(E_1) - c_O^S(E_2)] \]

\[ + 2\varepsilon_R \delta_R B[c_R^S(E_1) - c_R^S(E_2)] \log[\tau(E_1)/\tau(E_2)] \]  \hspace{1cm} (II-12)

As indicated, this general expression is independent of \( I_L(\text{in}) \), the intensity of the incoming beam, and also of \( L \). A particularly convenient choice of \( E_2 \) is a value at which no reaction takes place, denoted at \( E_O \), in which case the right hand side of Eq. II-12 becomes
\[ A(E_1) - A(E_0) = 2\varepsilon_0\delta_0 B[c_0^s(E_1) - c_0^o] + 2\varepsilon_R\delta_R B[c_R^s(E_1) - c_R^o] - \log[r(E_1)/r(E_0)] \] (II-13)

II-3. EXPERIMENTAL

All measurements were carried out at a near normal incidence angle using an all-quartz electrochemical cell, consisting of a cylinder fused to a flat optical window, and a Pine rotator/rotating gold electrode system (disk area: 0.164 cm²). The optical system employed (see Figure II-1) was similar to that developed in this laboratory for in situ reflection absorption magnetic circular dichroism⁶ except that the tungsten-halogen lamp was replaced by an ultra-stable arc Xenon lamp (USA 150-3, Optical Radiation Corp.). All experiments were performed in \( \text{K}_4\text{Fe(\text{CN})}_6/0.5 \: \text{M} \: \text{K}_2\text{SO}_4 \) aqueous solutions at room temperature. \( \text{K}_4\text{Fe(\text{CN})}_6 \) (Fisher, reagent grade) was recrystallized from water, and \( \text{K}_2\text{SO}_4 \) (Baker Analyzed reagent) was used as received.

For most of the runs, the monochromator was set at 420 nm, a wavelength at which \( \text{Fe(\text{CN})}_6^{3-} \) exhibits an absorption maximum and the absorptivity of \( \text{Fe(\text{CN})}_6^{4-} \) is negligibly small. This provides ideal conditions for verifying experimentally the predictions of the theoretical analysis (vide infra).

Reflection absorption data were acquired as the electrode potential was scanned linearly between 0.0 V and 0.4 V vs. SCE in a repetitive fashion by feeding the output signal of the photomultiplier into a signal
averager (Nicolet 1170). About ten cycles were often found sufficient to obtain an adequate signal-to-noise ratio. Measurements were conducted as a function of the concentration of the species in solution and the rotation rate.

II-4. RESULTS AND DISCUSSION

A number of conditions were chosen for the forced convection reflection absorption experiments so as to simplify somewhat the analysis of the data and thus test the predictions made by the theory. Specifically, (i) only the reduced form of the redox couple i.e. Fe(CN)$_6^{4-}$ was present in the bulk solution,

(ii) $\lambda$ was set at the absorption maximum of Fe(CN)$_6^{3-}$ in this spectral region, i.e. 420 nm, a wavelength at which $\varepsilon[\text{Fe(CN)}_6^{4-}]$ is essentially zero.

Furthermore, the potential range in which the redox transition occurs is within the double layer region of gold in this electrolyte; hence, $r(E_1) = r(E_0)$ and $\log[r(E_1)/r(E_0)]$ in Eq. II-13 becomes negligibly small.

Within this framework of approximations, Eq. II-13 can be rewritten as

$$A(E_1) - A(E_0) = 2\varepsilon_o\delta O B c_O^s(E_1)$$

$$= 3.610 \varepsilon_o B D_{O}^{1/3} v^{1/6} \Omega^{-1/2} c_{O}^s(E_1) \quad \text{(II-14)}$$

If $E_1$ is sufficiently positive for the oxidation of Fe(CN)$_6^{4-}$ to ensue, the current at the rotating disk electrode will be given by
\[ i = 0.620 F A D_R^{2/3} v^{-1/6} \Omega^{1/2} [c_R^o - c_R^s(E_1)] \]  

and therefore be proportional to \( c_O^s(E_1) \). This implies that the current is directly proportional to the difference in absorbance.

This is illustrated in Figure II-2, which gives a combined plot of the experimentally observed rotating disk current (dashed line) and \( A(E) - A(E_O) \) (as defined in Eq. II-14 above), as a function of the applied potential for the oxidation of 0.01 M \( \text{Fe(CN)}_6^{4+} \) in 0.5 M \( \text{K}_2\text{SO}_4 \) aqueous solutions at \( \Omega = 530 \text{ rpm} \). The optical and electrochemical data were acquired at scan rates of 100 mV/s and 2 mV/s, respectively. The latter was necessary to avoid current contributions due to the double layer (interfacial) capacity which become quite substantial at the scan rates employed for the optical studies. The diffusion coefficient of the ferrous species \((D_R)\) was obtained directly from the slope of the limiting current \((i_{\text{lim}})\) versus \(\Omega^{-1/2}\) plot using Levich equation

\[ i_{\text{lim}} = 0.620 n F A D_R^{2/3} v^{-1/6} \Omega^{1/2} c_R^o \]  

with \( n = 1, F = 96485 \text{ coul/mol}, A = 0.164 \text{ cm}^2, v = 0.01 \text{ cm}^2/\text{s}, c_R^o = 10 \mu\text{mol/cm}^3\), yielding a value for \( D_R = 6.4 \times 10^{-6} \text{ cm}^2/\text{s} \).

In order to compare quantitatively the current and absorbance difference, \( D_O \) was estimated from the relative magnitudes of \( D_O \) and \( D_R \) based on the data of Cahan and Villullas obtained in equimolar mixtures of \( \text{Fe(CN)}_6^{4+}/\text{Fe(CN)}_6^{3-} \) in neutral solutions \((D_O/D_R) = 1.15\).\(^7\) This yielded a value of \( D_O = 7.3 \times 10^{-6} \text{ cm}^2/\text{s}, \) which is in good agreement with literature data.\(^8\)

The theoretical conversion factor between the current (in \( \mu\text{A} \)) and
Figure II-2. Combined plot of the current (dashed line) and $A(E) - A(0 \text{ V})$, as defined in Eq. II-14, as a function of the applied potential for the oxidation of 0.01 M Fe(CN)$_6^{4-}$ in 0.5 M K$_2$SO$_4$ aqueous solutions. These curves were recorded at a rotation rate of 530 rpm, and a wavelength of 420 nm. The optical and electrochemical data were recorded at a scan rate of 100 mV/s and 2 mV/s, respectively. See text for other details.
the absorbance difference scales can be calculated based on the values of 
$D_O$ and the extinction coefficient for Fe(CN)$_6^{3-}$ ($\varepsilon_O = 1.14 \times 10^6$ mol$^{-1}$ cm$^2$) obtained by conventional transmission spectroscopy in the same 
electrolyte, yielding $[A(E) - A(E_0)] / i = 4.8 \times 10^{-5}$ $\mu$A$^{-1}$. It is precisely 
based on this theoretical factor that the left and right ordinates in Figure 
II-2 were drawn. It must be stressed that the scan rate employed for the 
acquisition of the spectral data was high and therefore to assume that the 
profiles can be represented by their steady state counterparts may be 
regarded as a rather poor approximation. Nevertheless, as shown in Figure 
II-2, the agreement between the two sets of data is good in the whole 
potential range.

Figure II-3 displays raw $[A(E) - A(0.0 \text{ V})]$ versus potential plots for 
the oxidation of 0.01 M K$_4$Fe(CN)$_6$/0.5 M K$_2$SO$_4$ aqueous solutions for 
three different rotation rates. These data were acquired at 200 mV/s and 
represents the cumulative sum of 16 consecutive scans. The solid curves 
were obtained after smoothing.

Plots of the absorbance difference, $A(0.4 \text{ V}) - A(0.0 \text{ V})$ (where a 
potential of 0.4 V is sufficiently positive for the current to be controlled 
purely by convective diffusion) versus $\Omega^{-1/2}$ were found to be linear (see 
Figure II-4) and thus in accordance with Eq. II-14. The magnitude of $\varepsilon_O$ 
calculated from the slopes of three independent experiments of this type 
$(1.12 (\pm 0.04) \times 10^6$ mol$^{-1}$cm$^2$) was in excellent agreement with the value 
obtained from conventional transmission spectra $(1.14 \times 10^6$ mol$^{-1}$ cm$^2$).
Figure II-3. $A(E) - A(0 \text{ V})$ versus potential plots for three different rotation rates. Scan rate: 200 mV/s. The dots and solid line represent the raw and smoothed data, respectively. See text for other details.
Figure II-4. Plot of $A(0.4V) - A(0 \text{ V})$ versus $\Omega^{-1/2}$ for 0.01 M Fe(CN)$_6^{4-}$ in 0.5 M K$_2$SO$_4$. 
Also in harmony with Eq. II-14 was the linear dependence of the absorbance difference on the concentration of the reactant shown in Figure II-5. The values of $e_O$ determined from these data, $1.04 \times 10^6$ mol$^{-1}$ cm$^2$ at 700 rpm and $1.06 \times 10^6$ at 530 rpm, were very close to those observed in the independent experiments.

As may be inferred from theoretical arguments, the sensitivity of the method for solution phase species decreases as the rotation rate is increased. This is not unexpected as the integrated profiles become less sensitive to $c^s$ (or, equivalently, to the applied potential), as the thickness of the diffusion boundary layer is reduced.

From a quantitative viewpoint, the results obtained in this study indicate that the coupling of reflection absorption UV-visible spectroscopy and the rotating disk electrode is sufficiently sensitive to detect the presence of the equivalent to a few monolayers of Fe(CN)$_6^{3-}$ in the diffusion boundary layer. For example, for $c_R^0 = 1 \times 10^{-5}$ mol/cm$^3$ at 1340 rpm, $A(0.4 \text{ V}) - A(0.0 \text{ V}) = 1.5 \times 10^{-2}$, which corresponds to $6.9 \times 10^{-9}$ mol/cm$^2$ being observed. Based on the experiments so far conducted, changes in absorbance as small as $5 \times 10^{-3}$ can be easily monitored upon co-adding sixteen voltammetric scans.

Finally, the reflection absorption technique described in this chapter offers a number of distinct advantages over the optically transparent/electrically insulating ring arrangement mentioned in the Introduction. Specifically,

(i) Any conventional, sufficiently reflecting, commercially
Figure II-5. Plot of the absorbance difference at the limiting current versus the concentration of Fe( CN)₆³⁺ in 0.5 M K₂SO₄ obtained at 700 (Δ) and at 500 rpm (O).
available rotating disk electrode can be used without the need of fiber optics technology for light irradiation and collection.

(ii) The analysis of the results does not rely on the actual area of the electrode being illuminated. Hence, the measurements are not subject to the geometrical uncertainties associated with the transparent insulating ring method.

(iii) The fluid is probed in a region in which the hydrodynamics can be approximated by a one-dimensional, as opposed to a two-dimensional model, and therefore the data analysis can be performed using simple analytical expressions.

(iv) The optical integration is effected along, and not away from the axis of rotation, a factor expected to increase the sensitivity.

(v) The fact that the electrode surface is irradiated makes it, in principle, possible to observe adsorbed reaction intermediates. Unlike the situation encountered for solution phase species, such as the one examined in this work, an increase in the rotation rate, and therefore in the number of adsorbed intermediates, should provide improved conditions for their detection and study.

Efforts to modify the present set up to include a rapid scan spectrophotometer will enable an expedient means of acquiring spectral data of (absorbing) species generated within the diffusion boundary layer, including intermediates and products and therefore help elucidate reaction mechanisms.
REFERENCES


CHAPTER III

TRANSIENT CONVECTIVE DIFFUSION
TO A ROTATING DISK ELECTRODE
AS MONITORED BY NEAR-NORMAL INCIDENCE
REFLECTION ABSORPTION UV-VISIBLE SPECTROSCOPY*

III-1. INTRODUCTION

The application of electrochemical techniques in the presence of well-defined hydrodynamic flow to the study of electrode processes is particularly advantageous, as proper account can be made of the effects associated with mass transfer on the observed reaction rates.\(^1\) The rotating disk (and ring-disk) electrode may be regarded as perhaps the most versatile and indeed the most popular of these methods as evidenced by its widespread use in a variety of electrochemical areas.\(^2\) Although considerable insight into the pathways of a growing number of heterogeneous electron transfer reactions has been gained by the use of this and other forced convection configurations, it is essential to employ spectroscopic methods to identify unambiguously adsorbed and/or solution phase intermediates and multiple reaction products. Not

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* This chapter has been published:
surprisingly, much effort has been devoted toward the development of *in situ*\(^3\) and *on line*\(^4\) spectroscopic techniques for the detection and quantitation of such species. The coupling of these methods to forced convection systems, however, has received only very limited attention.\(^5-7\)

In the last chapter, a novel approach was described in which the surface of a rotating disk electrode was used as a mirror to monitor changes in the absorptivity of an aqueous solution of \(K_4[Fe(CN)_6]\) (at a fixed wavelength in the visible region) associated with the electrochemical generation of \([Fe(CN)_6]^{3-}\). The results obtained indicated not only that such measurements are feasible, but also that the data are amenable to rigorous quantitative analysis. Unlike this earlier work, which was restricted to quasi-steady state conditions, the present contribution describes an extension of that technique to the analysis of transient convective diffusion using the oxidation of \([Fe(CN)_6]^{4-}\) as a probe redox reaction. As will be shown, excellent agreement has been obtained between theory and experiments, opening new prospects for the development of modulation schemes with high enough sensitivity to observe *directly* the spectrum of the diffusion boundary layer.

III-2. THEORETICAL CONSIDERATIONS

A. Hydrodynamics

The reflection absorption technique described in Chapter II
provides a measure of the total number of (absorbing) species in the path of the optical beam, or equivalently, the integral of the concentration profile \( c(y, t) \), where \( c \) is the concentration of the species of interest and \( y \) represents a coordinate normal to the electrode surface. For steady state conditions, \( c(y) \), expressed in appropriate dimensionless variables, is unique, and therefore, as shown in Chapter II, the mathematical treatment is relatively simple. This is not the case, however, for the corresponding transient situation, a factor that complicates considerably the theoretical analysis.

Within the framework of approximations specified elsewhere,\(^1\) the differential equation that governs transient convective diffusion to a rotating disk electrode is given in Eq. 1, Table III-I, where \( D \) is the diffusion coefficient, and \( \nu_y = -\alpha y^2 \Omega^{3/2} \nu^{-1/2} \) the axial fluid velocity, where \( \alpha = 0.51024 \), \( \nu \) is the kinematic viscosity and \( \Omega \) the rotation rate of the electrode.

Of particular interest here is to determine the time evolution of the concentration profile of the absorbing species (either the reactant or the product) following application of a potential step of a large enough magnitude for the concentration of the reactant to be reduced to zero at the interface. This involves solving Eq. 1 subject to the initial and boundary conditions given in Eq. 2 in Table III-1.

Solutions to this problem have been given for short times by Krylov and Babak\(^8\) in terms of parabolic cylinder functions, \( D_k(z) \), and for long times by Nisancioglu and Newman\(^9\) in terms of (numerically evaluated)
Table III-I. Transient Convective Diffusion to a Rotating Disk Electrode

Governing equation

\[ D \frac{\partial^2 c}{\partial y^2} - \nu_x \frac{\partial c}{\partial y} \frac{\partial c}{\partial t} = 0 \]  

(1)

Boundary conditions for concentration step problem

\begin{align*}
  c(0, t) &= 0 \\
  c(\infty, t) &= c_0 \\
  c(y, 0) &= c_0
\end{align*}

(2)

Short - time solution | Long - time solution

Dimensionless variables

\begin{align*}
  C &= \frac{c}{c_0}, \quad \tau = (DA^2)^{\frac{1}{3}} t, \quad x = \left(\frac{A}{D}\right)^{\frac{1}{3}} y \\
  \Theta &= \frac{c_0 - c}{c_0}, \quad \Theta = \omega \left(\frac{D}{\nu}\right)^{\frac{1}{3}} \left(\frac{a}{3}\right)^{\frac{2}{3}} t
\end{align*}

(3a)

\begin{align*}
  A &= a \left(\frac{\omega}{\nu}\right)^{\frac{1}{2}}, \quad z = x(2 \tau)^{\frac{1}{2}} \\
  \zeta &= \left(\frac{\alpha \nu}{3D}\right)^{\frac{1}{3}} \left(\frac{\omega}{\nu}\right)^{\frac{1}{2}} y
\end{align*}

(3b)

Convective diffusion equation

\begin{align*}
  \frac{\partial^2 C}{\partial z^2} + x^2 \frac{\partial C}{\partial x} \frac{\partial C}{\partial \tau} &= 0 \quad (4a) \\
  \frac{\partial^2 \Theta}{\partial \zeta^2} + 3 \zeta^2 \frac{\partial \Theta}{\partial \zeta} - \frac{\partial \Theta}{\partial \theta} &= 0 \quad (4b)
\end{align*}

(continued)
Table III-I. Transient Convective Diffusion to a Rotating Disk Electrode (continued)

<table>
<thead>
<tr>
<th>Boundary conditions</th>
<th>Dimensionless profile</th>
<th>Dimensionless flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C(0, \tau) = 0$</td>
<td>$\Theta(\zeta, \theta) = \Theta'' - \Theta'$</td>
<td>$j(\tau) = j(\infty) \left( 1 + \sum_{n=1}^{\infty} \frac{2\pi b_n^{(n)}}{\Gamma(-k/2)} \right)^{-1/2}$</td>
</tr>
<tr>
<td>$C(\infty, \tau) = 1$</td>
<td>$\Theta'' = \frac{1}{\Gamma(4/3)} \int_{\zeta}^{\infty} e^{-x^4} dx$</td>
<td>$j(\theta) = j(\infty) \left( \frac{\partial \Theta''}{\partial \zeta} \right)_{\zeta=0} - \frac{\partial \Theta'}{\partial \zeta} \theta_0$</td>
</tr>
<tr>
<td>$C(z, 0) = 1$</td>
<td>$\Theta' = \sum_{n=0}^{\infty} B_n Z_n(\zeta) e^{-\lambda_n \theta}$</td>
<td>(8b)</td>
</tr>
<tr>
<td>(5a)</td>
<td>(6a)</td>
<td>(8a)</td>
</tr>
</tbody>
</table>

$$C(z, \tau) = \sum_{n=0}^{\infty} \frac{3n}{2} G_n(z)$$

$$G_n(z) = e^{-\frac{z^2}{4}} \sum_{k=3n-1}^{3n-1} b_k^{(n)} D_k(z)$$

$$B_n = \int_0^1 \Theta'' Z_n(\zeta) d\zeta$$

$$j(\tau) = \frac{\alpha^3}{0.6 \pi \eta} \left[ 1 + \sum_{n=1}^{\infty} \frac{2\pi b_n^{(n)}}{\Gamma(-k/2)} \right]$$

$$\frac{j(\theta)}{j(\infty)} = \frac{3\alpha^3}{0.6 \pi \eta} \left( \frac{\partial \Theta''}{\partial \zeta} \right)_{\zeta=0} - \frac{\partial \Theta'}{\partial \zeta} \theta_0$$
eigenvectors and eigenfunctions of the associated Sturm-Liouville system. A brief summary of these two mathematical formalisms is given in the left and right panels of Table III-I, including the dimensionless variables appropriate for each treatment, as well as the dimensionless profiles and fluxes at the electrode surface. Explicit expressions for the coefficients $b_k^{(n)}$ may be found in the original literature.$^8$

B. Optics

Consider a rotating disk electrode immersed in a solution containing a non-absorbing electroactive species and polarized (at $t = 0$) at a potential $E_0$ such that no reaction occurs. If the potential is then stepped ($t > 0$) to a value sufficiently positive (or negative) for the species to undergo oxidation (or reduction) to generate an optically absorbing product, the change in the solution absorbance $A$ can be written as

$$A(t) - A(t = 0) = \log\left[\frac{I_L^{\text{out}}}{I_0^{\text{out}}}\right] = 2\varepsilon\int_0^L c dy + \log\frac{r(E_0)}{r(E)}$$  \hspace{1cm} (III-1)

$I_L^{\text{out}}$ in this equation is the time dependent intensity of the beam exiting the cell, $\varepsilon$ is the extinction coefficient of the species of interest and $r(E) = I_0^{\text{out}}/I_0^{\text{in}}$ represents the reflectivity loss at the specified potential, where $I_0^{\text{out}}$ and $I_0^{\text{in}}$ are the intensities of the beam just before and after reflecting from the electrode surface. The last term in Eq. III-1 is generally very small and can therefore be neglected. The reflection absorption technique developed in this laboratory (see Chapter II) makes it
possible to determine experimentally the right hand side of Eq. III-1 above and thus provide a means for a direct spectroscopic verification of the theory.

C. Electrochemistry

Also amenable to experimental determination is the current flowing through the working electrode, a quantity that can be recorded during spectral acquisition. This provides an independent means of testing the theory based on two different observables measured simultaneously. Expressions for the dimensionless flux, defined as $j/j_\infty$, based on the short- and long-time solutions are given in Eqs. 8a and 8b in Table III-I, respectively.

III-3. EXPERIMENTAL

All measurements were conducted using the same experimental set-up described in Chapter II which involves an all-quartz electrochemical cell, a Pine rotator/rotating gold electrode system (disk area: 0.164 cm$^2$) coupled to a near normal incidence UV-visible reflection absorption spectrophotometer, a PAR Model 173 potentiostat/galvanostat and a PAR Model 175 signal generator. Experiments were performed in 0.01 M $K_4Fe(CN)_6$ (Fisher, reagent, recrystallized) and 0.5 M $K_2SO_4$ (Baker Analyzed) aqueous solutions at room temperature. The monochromator
was set at 420 nm, a wavelength at which Fe(CN)$_6^{3-}$ exhibits an absorption maximum and the absorptivity of Fe(CN)$_6^{4-}$ is negligibly small. This provides ideal conditions for testing the predictions of the theoretical analysis (*vide infra*). A Ag/AgCl (BAS, W. Lafayette, IN) was used as a reference and a gold foil as a counter electrode.

Reflection absorption data were acquired as the electrode potential was stepped between 0.0 V vs. Ag/AgCl, a voltage at which no reaction takes place, and 0.4 V, a potential positive enough for the oxidation of the ferrous species to occur under complete mass transport control. The results obtained for each cycle, consisting of a forward and backward step, were coadded (16 to 32 cycles) using one channel of the signal averager (Nicolet 1170) for the optics and the other for the current. Data were collected for six different rotation rates.

III-4. RESULTS AND DISCUSSION

A. Numerical Evaluation of the Solutions of the Transient Convective Diffusion Equation for a Rotating Disk Electrode Under Concentration Step Conditions

a. Concentration Profiles

*Short-time Domain.* - Values for the various parabolic cylinder functions (including the error function) were determined by numerical integration of Eqs. 8.3.(3) (for $k < 0$) and 8.3.(4) (for $k > -1$) in Ref. 10. A
comparison between the calculated values and those provided in Ref. 11 yielded excellent results. Dimensionless concentration profiles for selected values of $\tau$ are shown in Figure III-1A. As indicated, the curves for large values of $\tau$ oscillate providing evidence that in that domain the series solution does not appear to converge. Certain aspects of this problem have been pointed out earlier in the literature\textsuperscript{12} and will not be discussed further here.

**Long-time Domain.** - The eigenfunctions $Z_n(\zeta)$ for $n = 0$ to 9 were evaluated using the IMSL routine DVERK in a VAX 11/785 computer based on the eigenvalues listed in Ref. 9, Table 1, by specifying only the last two boundary conditions, yielding for $Z_n(\zeta)$ with $n = 0$ to 2 identical results to those given in Figure 1 in that reference.

Dimensionless concentration profiles for selected values of $\theta$ are shown in Figure III-1B. In direct analogy to the behavior found for the solutions valid for short times, the long-term solutions at short times also undergo oscillations.

The two formalisms yielded (essentially) identical results in an intermediate time domain, specifically $0.02 < \tau < 0.5$, or using the conversion factor ($\tau = 3^{2/3}\theta$), $0.01 < \theta < 0.24$.

Accurate transient concentration profiles based on the two solutions spanning a wide range of times are shown in Figure III-2A. These were used to calculate (numerically) the corresponding transient integral profiles involved in the analysis of the spectroscopic data (Figure III-2B).
Figure III-1. (A) Theoretical concentration profiles obtained using the short-time solution (see Eq. 6a, Table III-1) for $\tau = 0.03$ (Curve a), $\tau = 0.1$ (Curve b) and $\tau = 0.624$ (Curve c).

(B) Theoretical concentration profiles obtained using the long-time solution (see Eq. 6b, Table III-1) for $\theta = 0.0024$ (Curve a), $\theta = 0.096$ (Curve b) and $\theta = 0.48$ (Curve c).
Figure III-2. (A) Exact concentration profiles obtained using the short- and long-time solutions, for (from left to right) $\tau = 0.01, 0.03, 0.1, 0.2, 1.0$ and steady state (dashed line). (B) Theoretical integral concentration profiles vs. time using the data shown in A; The dashed and solid lines were obtained from the short-time and long-time solutions.
b. Surface Fluxes

Figure III-3 gives plots of $j/j_\infty$ vs. $\tau$ calculated on the basis of the short-, and long-time solutions given in Eqs. 8a and 8b, Table III-I. As clearly shown, the two approaches yield essentially identical values in the range $0.05 < \tau < 1$ (or $0.024 < \theta < 0.5$).

B. Comparisons Between Theory and Experiment

Figure III-4 shows $[A(t) - A(t = 0)]$ vs. $t$ curves obtained for three different rotation rates. The relationship between the dimensionless and actual integral profile is given by:

$$\int (1-C)d(\tau^{1/2}) = a^{1/3}(\Omega/2)^{1/2} D^{-1/3} \nu^{-1/6} \int cdy$$  \hspace{1cm} (III-2)

Also shown in this figure are the theoretical results obtained from the universal profile shown in Figure III-2B using Eqs. III-1 and III-2 based on accepted values of the extinction coefficient for $[Fe(CN)_6]^{3-}$ (1.14 x $10^6$ mol$^{-1}$ cm$^{-2}$), diffusion coefficient (7.3 x $10^{-6}$ cm$^2$/s), kinematic viscosity (0.01 cm$^2$/s), and prescribed rotation rates (radian/s). The agreement between theory and experiment over the whole range of rotation rates examined is excellent. In every case, however, the theoretical curves were found to lie slightly above the experimental ones. A similar trend was also observed in the corresponding $j/j_\infty$ vs. $t$ curves shown in Figure III-5. The fact that the two independently (albeit simultaneously) measured observables yield results which deviate in the same direction suggests that the theoretical model herein described
Figure III-3. Comparison between the theoretical dimensionless surface fluxes obtained from the short- (Eq. 8a, Table III-I) (see dashed line) and long-time (Eq. 8b, Table III-I) (see solid line) solutions.
Figure III-4. Experimental (difference) absorbance, \([A(t) - A(t = 0)]\) vs. \(t\) obtained for \(\Omega = 400\) (Curve a), 650 (Curve b) and 1400 rpm (Curve c). The dashed lines are the corresponding theoretical curves based on the analysis presented in this chapter.
Figure III-5. Experimental dimensionless flux, $j/j_m$ vs. $t$ obtained for $\Omega = 400$ (Curve a), 1000 (Curve b) and 2500 rpm (Curve c). The dashed lines are the corresponding theoretical curves based on the analysis presented in this chapter.
represents a good although not extremely accurate approximation.

From an overall perspective, the possibility of quantitatively monitoring transient convective diffusion to a rotating disk electrode is expected to open new prospects for the development and implementation of concentration, or equivalently, potential modulation schemes, to increase the spectral sensitivity. As can be shown, the derivative of the optical signal (at a specific wavelength) with respect to the concentration of a given species is proportional to its extinction coefficient (at that specific wavelength). Hence, a plot of such derivative-like signal as function of wavelength should reproduce the conventional spectra for that species in the diffusion boundary layer.

REFERENCES


CHAPTER IV

POTENTIAL MODULATION NORMAL INCIDENCE REFLECTION ABSORPTION UV-VISIBLE SPECTROSCOPY UNDER FORCED CONVECTION: THEORETICAL ASPECTS*

IV-1. INTRODUCTION

The development of *in situ* spectroelectrochemical techniques in the presence of convective flow is expected to provide insight into the nature of intermediates and products of a variety of electrochemical reactions and thus shed light into mechanistic aspects of processes of technological and fundamental importance, including electrodeposition and electrocatalysis. The modulation strategies involving such variables as the electrode potential, the rotation rate of a disk electrode, and the wavelength of the incident light can markedly increase the sensitivity of many of these methods. Despite these advantages, no attempts have yet been made to combine modulation and *in situ* spectroscopic techniques under well-defined hydrodynamic conditions.

This chapter will present theoretical aspects of potential modulated normal incidence UV-visible reflection absorption spectroscopy at a rotating disk electrode (RDE). As will be shown, the mathematical

* This chapter has been partially published: M. Zhao and D. A. Scherson, *J. Electrochem. Soc.*, 140 (1993) 1671.
equations that relate the observed optical signal to the actual spectra of species present in the diffusion boundary layer can be expressed in terms of approximate solutions of the transient convective diffusion equation in the precise domain of perturbation frequencies in which the method is expected to be most sensitive. The excellent agreement obtained between theory and experiment for potential step transient measurements involving the same forced convection/optical spectroscopy arrangement (see Chapters II and III) strongly suggests that the modulation scheme herein described is capable of providing highly quantitative information.

IV-2. THEORY

A. Optics

According to elementary spectroscopy, the attenuation in the intensity $I$, of a beam of light traveling along an arbitrary axis $y$, through a media containing a single absorbing species $C$, may be written in differential form as follows:

$$-dI = \varepsilon (\lambda) \ k I(y, t) \ c(y, t) \ dy$$

(IV-1)

where $c(y, t)$ is the concentration of $C$, $\varepsilon$ is the extinction coefficient (cm$^2$/mol), a quantity that depends on the wavelength of the radiation $\lambda$, and $k = 2.3026$. As indicated, $c$, and therefore $I$, have been written as explicit functions of time (in addition to position) to account for variations in the magnitudes of these functions introduced by external temporal
perturbations.

Of particular interest here is the total attenuation of a beam that enters through the (flat) bottom of an electrochemical cell \( y = L \) along the axis of rotation of a RDE, reflects off the electrode surface \( y = 0 \) and exits the cell along the same axis, but in opposite direction.\(^1\) Although the actual measurements are not performed with the beam precisely normal to the surface, the angle of incidence (as measured with respect to the axis of rotation) can be chosen to be small enough for its effect on the theory to be neglected.

The intensity of the beam impinging on the electrode surface \( I_{0}(\text{in}) \), can be calculated by integrating Eq. IV-1 to yield \(^1\)

\[
I_{0}(\text{in}) = I_{L}(\text{in}) \exp\left[\varepsilon(\lambda)k\int_{L}^{0} c(y, t)\,dy\right]
\]  
(IV-2)

On this basis, the intensity of the light exiting the cell, \( I_{L}(\text{out}) \) may be shown to be given by

\[
I_{L}(\text{out}) = r(\lambda, E) I_{L}(\text{in}) \exp\left[-2\varepsilon(\lambda)k\int_{0}^{L} c(y, t)\,dy\right]
\]  
(IV-3)

where \( r = I_{0}(\text{out})/I_{0}(\text{in}) \) accounts for the reflection loss at the RDE surface, a parameter that depends on the energy of the beam and on the electrode potential, \( E \). For simplicity, however, \( r \), for a fixed \( \lambda \), will be assumed to be constant over the narrow range of potentials involved in the modulation. A more general treatment that includes electroreflectance effects is given in Appendix IV-A.

Consider a situation in which the RDE is polarized at a potential \( E \),
in a range in which \( C \) is generated below limiting current conditions, so that \( c(y, t) \) can be represented by a (time-independent) steady state profile, \( \bar{c}(y) \). If a sinusoidal voltage of small amplitude is then applied to the RDE, the concentration at each point along the axis of rotation will shortly thereafter relax to a steady oscillatory regime. Under these conditions, \( c(y, t) \) can be expressed as the sum of a steady state, \( \bar{c}(y) \), and an oscillatory, \( \bar{c}(y,t) \), contributions

\[
c(y, t) = \bar{c}(y) + \bar{c}(y, t)
\]

(IV-4)

Therefore \( I_L(\text{out}) \), normalized by the intensity of the light at steady state \( \bar{I}_L(\text{out}) \) (or \( I_{dc} \)), may be shown to be given by

\[
\frac{I_L(\text{out})}{\bar{I}_L(\text{out})} = \exp\left[-2\varepsilon(\lambda)k\int_0^L \bar{c}(y, t)dy\right]
\]

(IV-5)

Since the changes in \( c(y, t) \) induced by the sinusoidal perturbation are small, the argument of the exponential in Eq. IV-5 can be approximated by the first two terms in the Taylor series expansion yielding after rearrangement

\[
(\bar{I}_L(\text{out}) - I_L(\text{out}))/\bar{I}_L(\text{out}) = \frac{I_{ac}}{I_{dc}} = 2\varepsilon(\lambda)k\int_0^L \bar{c}(y, t)dy
\]

(IV-6)

The sinusoidally varying optical response \( I_{ac} \), normalized by \( I_{dc} \), can be measured experimentally using conventional lock-in amplifier techniques, whereas the time dependent part of the integral on the right hand side of the equation, for low perturbation frequencies, can be expressed in terms of approximate solutions reported earlier in the
literature\textsuperscript{6} (\textit{vide infra}). This provides a convenient means of determining quantitatively the contributions of $C$ to the spectrum of the diffusion boundary layer.

B. Hydrodynamics

Within the framework of approximations described in detail elsewhere,\textsuperscript{7} the equation that governs transient convective diffusion to a rotating disk electrode can be written as

$$\frac{\partial^2 c}{\partial \zeta^2} + 3\zeta^2 \frac{\partial c}{\partial \zeta} - \frac{\partial c}{\partial \theta} = 0 \quad (\text{IV-7})$$

where

c, as before, (and without loss of generality) is the concentration of the electrogenerated, optically absorbing species in mol/cm\textsuperscript{3}

$\theta = t \Omega D(a v/3D)^{2/3}/ v$ is the dimensionless time

$\Omega$ is the rotation rate of the disk in rad/s

$\zeta = (\Omega/v)^{1/2}(a v/3D)^{1/3} y$ is the dimensionless distance along $y$

$a = 0.51023$, and all other symbols have their usual meaning.

Of particular concern here are solutions of Eq. IV-7 of the form $c = \bar{c} + \tilde{c} = \bar{c} + A e^{i \omega K}$, where $A e^{i \omega K}$ is the amplitude of the time varying concentration, $\bar{c}$, $K = \omega \sqrt{3D/(a v)}^{2/3}/\Omega D$ is a dimensionless frequency and $\omega$ the potential modulating frequency in rad/s. This expression for $c$ can be replaced in Eq. IV-7 to yield
\[
\frac{\partial^2 \psi}{\partial \zeta^2} + 3 \zeta^2 \frac{\partial \psi}{\partial \zeta} - jK \psi = 0
\]  \hspace{1cm} (IV-8)

subject to the boundary conditions
\[
\psi = 1 \text{ at } \zeta = 0 \text{ and } \psi \to 0 \text{ as } \zeta \to \infty
\]  \hspace{1cm} (IV-9)

If \( jK \) is regarded as a generalized complex parameter, the formal inverse Laplace transform (with respect to this parameter) of Eq. IV-8 can be shown to yield Eq. IV-7 subject to the same boundary conditions for the concentration step problem. Hence, the Laplace transform of the solutions of this time domain problem are precisely the solutions of Eq. IV-8 subject to the conditions specified in Eq. IV-9, which (upon an appropriate variable transformation) can be used to evaluate the integral on the right hand side of Eq. IV-6.

IV-3. RESULTS AND DISCUSSION

A. Calculation and Comparison of Exact and Long-Time Solutions

Figure IV-1 shows plots of the exact real and imaginary parts of \( \psi \) as a function of \( \zeta \) for selected values of \( K \) determined using a commercially available routine (see Appendix IV-B). The change in sign of both these functions is not an artifact of the numerical calculations, as the same phenomenon was observed for stagnant media \( i.e. \Omega = 0 \), in the high frequency regime for which solutions can be obtained in terms of simple analytical expressions (see Appendix IV-C). This is illustrated in
Figure IV-1. Plots of the exact real and imaginary parts of $\psi$ as a function of $\zeta$ for selected values of $K$. 
Panel B, Figure IV-2, which shows that at high frequencies \((K = 60)\) both \(\text{Re}\psi\) and \(\text{Im}\psi\) as a function of the actual axial distance \(y\), for the stagnant (dashed line) and forced convection (solid line) yielded essentially the same result. This is unlike the behavior observed in the low frequency domain (see Panel A, Figure IV-2), for which the two solutions were markedly different.

Particularly important from an experimental viewpoint are solutions of Eq. IV-7 valid for long times, as the corresponding Laplace transforms provide accurate representations of the behavior of the system in a domain of frequencies low enough to enhance the optical response and hence increase the sensitivity \(\textit{vide infra}\).

Based on the formalism introduced by Nisancioglu and Newman\(^6\) the solution for the concentration step problem valid for long times, denoted as \(\Theta\), can be expressed as the difference between the steady state \((\Theta^{ss})\) and transient \((\Theta^t)\) contributions, \(i.e.\)

\[
\Theta = \Theta^{ss} - \Theta^t = \frac{1}{\Gamma(4/3)} \int_x^\infty \exp(-x^3) \, dx - \sum_{n=0}^\infty B_n Z_n(\zeta) \exp(-\lambda_n \theta)
\]  

(IV-10)

where \(Z_n(\zeta)\), \(\lambda_n\) and \(B_n\) are the eigenfunctions, eigenvalues and coefficients of the appropriate Sturm-Liouville system, respectively, which upon Laplace transformation yields

\[
L\{\Theta(\zeta, \theta)\} = \Psi(\zeta, K) = \frac{1}{\Gamma(4/3)} \int_x^\infty \exp(-x^3) \, dx
\]

\[
- \sum_{n=0}^\infty B_n Z_n(\zeta) [K^2/(\lambda_n^2 + K^2)] - \int \sum_{n=0}^\infty B_n Z_n(\zeta) [K\lambda_n/(\lambda_n^2 + K^2)]
\]  

(IV-11)
Figure IV-2. Plots of $\text{Re}\psi$ and $\text{Im}\psi$ for $K = 1.2$ (Panel A, $\omega = 13.89$ rad. s$^{-1}$) and $K = 60$ (Panel B, $\omega = 694.4$ rad. s$^{-1}$) as a function of the real axial distance for $\Omega = 0$ (dashed line) and $\Omega = 377$ rad/s (3600 rpm) (solid line).
Figure IV-3 compares the real and imaginary components of \( \Theta(\zeta; K) \) as a function of \( \zeta \) determined from Eq. IV-11 with the exact numerical solution for \( K = 6, 20 \) and \( 60 \), where the functions \( Z_n(\zeta) \) were calculated using the method described in Ref. 2. Although significant deviations could be observed for high frequencies particularly for \( \text{Im} \psi \), the agreement for \( K \) values up to 20 was excellent.

Of direct relevance to the problem under analysis, however, are the magnitudes of the real and imaginary components of the integral of the dimensionless concentration profile.* As shown in Figures IV-4 and IV-5, the approximate solution reproduces very accurately the exact values for \( K < 20 \) (see also Table IV-I). Particularly noteworthy is the limiting angle of \(-45^\circ\) for \( K > 40 \) (see dotted line in Figure IV-5) as should be expected for a stagnant media in the whole frequency domain (see Appendix IV-C).

The good harmony between the approximate and exact treatments in the low frequency range for the forced convection system is unlike that observed for the Warburg impedance function, i.e. \( L[-1/\psi'(0)] \), evaluated from the same long-time solution, for which the calculated values are found to differ substantially from the exact ones even for very low frequencies (see Table IV-II). It may be noted in this regard, however, that much better agreement has been found using \( Z_n(\zeta) \), \( \lambda_n \) and \( B_n \) for flux step boundary conditions by taking advantage of the reciprocity relationships between the solutions of the two problems.10

* This integral reaches a limiting value for \( \zeta = 2 \). Therefore it is reasonable to replace the upper limit by infinity.
Figure IV-3. Comparison of the real and imaginary components of $\psi(\zeta; K)$ as a function of $\zeta$ for $K = 6$, 20 and 60. Solid lines are the exact solutions whereas the dashed lines were obtained from Eq. IV-11.
Figure IV-4. Plots of the real and imaginary components of the integral of the dimensionless concentration profile for the exact (solid line) and long-time (dashed line) solutions.
Figure IV-5. Plots of the real and imaginary components of the integral of the dimensionless concentration profile in the complex plane: • - exact and Δ - long time solutions.
Table IV-I. Solutions for Real and Imaginary Parts and Absolute Value of $\int_0^\infty \Psi d\zeta$

<table>
<thead>
<tr>
<th>K</th>
<th>$\int_0^\infty \Re \Psi d\zeta$</th>
<th>$\int_0^\infty \Im \Psi d\zeta$</th>
<th>$\int_0^\infty \Psi d\zeta$</th>
<th>$\int_0^\infty \Re \Psi d\zeta$</th>
<th>$\int_0^\infty \Im \Psi d\zeta$</th>
<th>$\int_0^\infty \Psi d\zeta$</th>
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<td>0.50447</td>
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Table IV-II. Solutions for the Real and Imaginary Parts of $-1/\Psi'(0)$

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<th>Long-time Solution</th>
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<td>$\text{Im}{-1/\Psi'(0)}$</td>
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</table>
B. Potential Modulated Reflection Absorption Normal Incidence UV-Visible Spectroscopy

From a practical viewpoint, all the spectroscopic information is contained in the energy dependence of the extinction coefficient. Therefore it is useful to derive an explicit expression for this quantity based on the formalism developed in the previous sections. As can be shown from Eq. IV-6

$$\varepsilon(\lambda) = \left( I_{ac} / I_{dc} \right) \left[ 2k \int_0^\infty \tilde{c}(y, t) dy \right]^{-1} \quad \text{(IV-12)}$$

or equivalently

$$\varepsilon(\lambda) = \left( I* / I_{dc} \right) \exp\left[ j(K\Theta + \phi) \right] / \left[ 2k\gamma A* \exp(jK\Theta) \int_0^\infty \Psi(\zeta) d\zeta \right] \quad \text{(IV-13)}$$

$I_{ac}$ in this equation has been replaced by $I* \exp[j(K\Theta + \phi)]$, where $I*$ is the amplitude of the time varying light intensity and $\phi$ is the phase (vide infra), and $\gamma$ is the factor that converts $y$ into the dimensionless variable $\zeta$. Since $\varepsilon(\lambda)$ is real, the phase in Eq. IV-13 can be shown to be given by

$$\phi = \arctan \left( \frac{\int_0^\infty \text{Im} \Psi d\zeta}{\int_0^\infty \text{Re} \Psi d\zeta} \right) \quad \text{(IV-14)}$$

A plot of the phase as function of $K$ is shown in Figure IV-6. On this basis, $\varepsilon(\lambda)$ can be written in three equivalent forms, namely
Figure IV-6. Plot of the phase $\phi$, as function of the dimensionless frequency $K$. 
\[ \varepsilon(\lambda) = \frac{(I^* / I_{dc})(2k\gamma A *)^{-1}}{\cos \phi / \int_0^\infty \text{Re} \, \Psi \, d\zeta} \]

\[ = \frac{(I^* / I_{dc})(2k\gamma A *)^{-1}}{\sin \phi / \int_0^\infty \text{Im} \, \Psi \, d\zeta} \]  

\[ = \frac{(I^* / I_{dc})(2k\gamma A *)^{-1}}{\left| \int_0^\infty \Psi \, d\zeta \right|} \]  

(IV-15)

A plot of \( \left| \int_0^\infty \Psi \, d\zeta \right| \) as a function of \( K \) is shown in Figure IV-7 and the corresponding values for selected dimensionless frequencies either exact or obtained from the long-time approximation are listed in Table IV-1.

C. Absorbing Reactant and Product

According to Eq. IV-12, the ratio of the amplitude of the ac component, \( I_{ac} \), and the magnitude of the dc component of the optical signal \( I_{dc} \) is related to the energy dependent extinction coefficient via the equation

\[ \frac{I_{ac}}{I_{dc}} = 2k\varepsilon(\lambda) \int_0^\infty \tilde{c}(y, t) \, dy \]  

(IV-16)

In the case of two absorbing species, this equation may be shown to yield

\[ \frac{I_{ac}}{I_{dc}} = 2k\varepsilon_1(\lambda) \int_0^\infty \tilde{c}_1(y, t) \, dy + 2k\varepsilon_2(\lambda) \int_0^\infty \tilde{c}_2(y, t) \, dy \]  

(IV-17)

where \( \tilde{c}_i \) is the oscillatory concentration expressed in terms of a
Figure IV-7. Plot of $|\int_0^\infty \Psi d\zeta|$ as a function of $K$, based on the exact solutions.
dimensionless time $\theta_i$, dimensionless frequency $K_i$, and spatially dependent function $\Psi_i$

$$\tilde{c}_i = A_i \ast \Psi_i \exp(jK_i\theta_i) \quad (IV-18)$$

Similarly,

$$I_\infty = I* \exp[j(K\theta + \phi)] \quad (IV-19)$$

Hence, replacing Eqs. IV-18 and IV-19 into Eq. IV-17 one obtains

$$\left(\frac{I*}{I_{de}}\right) \exp(j\phi) = 2K\epsilon_1(\lambda)A_1 \int_0^\infty \psi_1 dy + 2K\epsilon_2(\lambda)A_2 \int_0^\infty \psi_2 dy \quad (IV-20)$$

It may be noted that for two redox related species at the standard redox potential the concentrations of the two species are equal and therefore, $A_{-1} = -A_{+2}$.

Eq. IV-20 can be rewritten in term of quantity $P_i = 2K\epsilon_i(\lambda)\gamma_iA_i$, as follows

$$\left(\frac{I*}{I_{de}}\right) \left(\cos \phi + j \sin \phi\right) = (P_1 \int_0^\infty \text{Re}(\Psi_1) d\zeta + P_2 \int_0^\infty \text{Re}(\Psi_2) d\zeta)$$

$$+ j(P_1 \int_0^\infty \text{Im}(\Psi_1) d\zeta + P_2 \int_0^\infty \text{Im}(\Psi_2) d\zeta) \quad (IV-21)$$

which yields two equivalent expressions

$$\left(\frac{I*}{I_{de}}\right) \cos \phi = P_1 \int_0^\infty \text{Re}(\Psi_1) d\zeta + P_2 \int_0^\infty \text{Re}(\Psi_2) d\zeta \quad (IV-22)$$

$$\left(\frac{I*}{I_{de}}\right) \sin \phi = P_1 \int_0^\infty \text{Im}(\Psi_1) d\zeta + P_2 \int_0^\infty \text{Im}(\Psi_2) d\zeta \quad (IV-23)$$
The phase $\phi(\lambda)$ can be calculated from

$$\phi(\lambda) = \arctan \left[ \frac{P_1 \int_{\lambda_0}^{\lambda_1} \text{Im}(\Psi) \, d\zeta + P_2 \int_{\lambda_0}^{\lambda_1} \text{Im}(\Psi) \, d\zeta}{P_1 \int_{\lambda_0}^{\lambda_1} \text{Re}(\Psi) \, d\zeta + P_2 \int_{\lambda_0}^{\lambda_1} \text{Re}(\Psi) \, d\zeta} \right]$$  \hspace{1cm} (IV-24)

D. Sensitivity Considerations

Based on Eq. IV-15, the ratio $(I^*/I_{dc})$ can be expressed in terms of real variables as follows

$$\left(\frac{I^*}{I_{dc}}\right) = 2\varepsilon(\lambda) \lambda^* k \left(\frac{3D}{\alpha v}\right)^{1/3} \nu^{1/2} \left| \int_{0}^{\lambda_0} \Psi \, d\zeta \Omega^{-1/2} \right|$$  \hspace{1cm} (IV-25)

A plot of $\left| \int_{0}^{\lambda_0} \Psi \, d\zeta \Omega^{-1/2} \right|$ as a function of $\omega$ for different values of $\Omega$ is shown in Figure IV-8. As indicated, this function reaches a limiting value as $\omega$ decreases and becomes independent of $\Omega$ for higher modulation frequencies, i.e. $\omega > 100$. This is more clearly illustrated in Figure IV-9, in which $\left| \int_{0}^{\lambda_0} \Psi \, d\zeta \Omega^{-1/2} \right|$ is displayed as a function of $\Omega$ for selected values of $\omega$.

An estimate of the magnitude of $(I^*/I_{dc})$ can be obtained based on the values of the parameters in Eq. IV-25. Assuming $\left| \int_{0}^{\lambda_0} \Psi \, d\zeta \Omega^{-1/2} \right| = 0.05$ (see Figure IV-8), $D = 10^{-5}$ cm$^2$/s, and $\nu = 0.01$ cm$^2$/s, Eq. IV-16 yields

$$(I^*/I_{dc}) = 4 \times 10^{-3} \varepsilon(\lambda) \lambda^*$$  \hspace{1cm} (IV-26)

As shown in Appendix IV-D, the maximum value of $dE/dc$ for a fast redox
couple is obtained for $E = E^0$, i.e., the concentrations of the reduced and oxidized species at the electrode surface are the same. Hence, if the electrode is polarized at $E^0$, the amplitude of the potential modulation, $\Delta E$, is related to the corresponding amplitude for the concentration modulation, $\Delta c = A^*$, via the expression

$$A^* = (nFce_0/4RT)\Delta E$$

(IV-27)

where $c_0$ is the initial concentration of a solution containing either the oxidized or reduced species. For $c_0 = 10$ mM and a potential modulation amplitude of $5$ mV, and assuming $n = 1$ and $T = 298$ K, $A^* = 5 \times 10^{-7}$ mol/cm$^3$, hence

$$(I^*/I_{dc}) = 2 \times 10^{-9}\varepsilon(\lambda)$$

(IV-28)

Experiments have shown (see Chapter V) that values of $(I^*/I_{dc})$ as small as $2 \times 10^{-4}$ can be measured with fairly conventional instrumentation. This indicates that, under the specified conditions, species with molar absorptivities on the order of hundreds could be easily detected.

A complete experimental verification of the theory herein described is reported in the next chapter.

APPENDIX IV-A

In the limit of small perturbations, the equation

$$I_L(\text{out}) = r(\lambda, E) I_L(\text{in}) \exp[-2\varepsilon(\lambda)k \int_0^L c(y, t)dy]$$

(IV-A1)
Figure IV-8. Plot of the exact values of $\int_0^\infty \Psi d\zeta \Omega^{-1/2}$ as a function of $\omega$ for different values of $\Omega$.
Figure IV-9. Plot of the exact values of $\int_0^\theta \Psi d\zeta \Omega^{-1/2}$ as a function of $\Omega$ for different values of $\omega$. 
can be linearized by a simple two variable expansion in Taylor's series (in incremental form) about the steady state, namely

\[ f(a+h, b+k) = f(a+b) + \left( h \frac{\partial}{\partial x} + k \frac{\partial}{\partial y} \right) f(x, y) \bigg|_{x=a, y=b} + \cdots \quad (\text{IV-A2}) \]

where \( x = E, \)
\[ y = -2\varepsilon(\lambda)k \int_0^E c(y, t) dy, \]
\[ a = \bar{E}, \]
\[ b = -2\varepsilon(\lambda)k \int_0^E \bar{c}(y) dy, \]
\[ f(a+h, b+k) = I_L(\text{out}) \text{ and} \]
\[ f(a, b) = I_L(\text{out}). \text{ Hence} \]

\[ \left( I_L(\text{out}) - I_L(\text{out}) / I_L(\text{out}) \right) \]
\[ = \left( -1 / \bar{r}(\lambda, E) \right) \left( \frac{\partial r(\lambda, E)}{\partial E} \right) \bigg|_{E=\bar{E}} (E - \bar{E}) \]
\[ + 2\varepsilon(\lambda)k \int_0^E [c(y, t) - \bar{c}(y)] dy \quad (\text{IV - A3}) \]

where \( (1 / \bar{r}(\lambda, E)) \left( \frac{\partial r(\lambda, E)}{\partial E} \right) \bigg|_{E=\bar{E}} \) is the electromodulation reflection coefficient \( \rho \), at \( \bar{E}. \) For the problem in question \([c(y, t) - \bar{c}(y)]\) is precisely \( \bar{c}(y, t) \) and similarly \( E - \bar{E} = \bar{E}. \) It thus follows that when \( \rho \) is small (as was assumed in this work) the first term vanishes and Eq. VI-A3 reduces to Eq. IV-6.
APPENDIX IV-B

Numerical solutions of Eq. IV-8 for selected values of $K$ and subject to the boundary conditions in Eq. IV-9 were obtained using the IMSL routine DTPTB, which solves a system of differential equations with boundary conditions at two points, using a multiple shooting method. Specifically, Eq. IV-8

$$\frac{\partial^2 \Psi}{\partial \zeta^2} + 3 \zeta^2 \frac{\partial \Psi}{\partial \zeta} - jK \Psi = 0$$

subject to the boundary conditions in Eq. IV-9

$$\Psi = 1 \text{ at } \zeta = 0 \text{ and } \Psi \to 0 \text{ as } \zeta \to \infty$$

can be expressed as two coupled second-order differential equations with real coefficients involving the real and imaginary parts of the complex function $\Psi(\zeta)$, i.e. $\text{Re}\Psi$ and $\text{Im}\Psi$, respectively, as follows

$$\frac{\partial^2 \text{Re}\Psi}{\partial \zeta^2} + 3 \zeta^2 \frac{\partial \text{Re}\Psi}{\partial \zeta} + K \text{Im}\Psi = 0 \tag{IV-B1}$$

$$\frac{\partial \text{Im}\Psi}{\partial \zeta} + 3 \zeta^2 \frac{\partial \text{Im}\Psi}{\partial \zeta} - K \text{Re}\Psi = 0 \tag{IV-B2}$$

subject to

$$\text{Re}\Psi = 1 \text{ at } \zeta = 0$$

$$\text{Im}\Psi = 0 \text{ at } \zeta = 0 \tag{IV-B3}$$

$$\text{Re}\Psi \to 0 \text{ as } \zeta \to \infty$$

$$\text{Im}\Psi \to 0 \text{ at } \zeta \to \infty \tag{IV-B4}$$
No differences were found between the numerical solutions obtained for \( \zeta = 2 \) and \( \zeta = 3 \), indicating that these finite boundary conditions satisfy the limits specified above.

APPENDIX IV-C

According to Fick's second law, diffusion to an infinite plane electrode in a stagnant media can be expressed as

\[
\frac{\partial c}{\partial t^*} = \frac{\partial^2 c}{\partial y^2}
\]  

(IV-C1)

where \( t^* = D t \). Consider, as before, solutions of \( c(y, t) \) of the form \( c = \bar{c} + \tilde{c} = \bar{c} + A^* \Psi \exp \left( j \omega^* t^* \right) \), where \( \omega^* = \omega / D \). Hence upon replacing this expression in Eq. IV-C1 one obtains

\[
\frac{\partial^2 \Psi}{\partial y^2} - j \omega^* \Psi = 0
\]  

(IV-C2)

with boundary conditions

\[
\begin{align*}
\Psi &= 1 \text{ at } y = 0 \\
\Psi &= 0 \text{ as } y \to \infty
\end{align*}
\]  

(IV-C3)

This equation can be solved analytically to yield

\[
\Psi = \left\{ \exp \left[ -\left( \frac{\omega^*}{2} \right)^{1/2} y \right] \right\} \left[ \cos \left( \frac{\omega^*}{2} \right)^{1/2} y - j \sin \left( \frac{\omega^*}{2} \right)^{1/2} y \right]
\]  

(IV-C4)
It thus follows from this expression that

\[ \int_0^a \text{Re } \Psi dy = (2 \omega *)^{-1/2} \]
\[ \int_0^a \text{Im } \Psi dy = -(2 \omega *)^{-1/2} \quad (\text{IV-C5}) \]

**APPENDIX IV-D**

For the problem under analysis, the Nernst equation can be written as

\[ E = E^0 + \frac{RT}{nF} \ln \left( \frac{c}{c_o - c} \right) \quad (\text{IV-D1}) \]

where \( c \) represents the surface concentration of the oxidized species. Hence, the rate of change of \( E \) with concentration is given by

\[ \frac{dE}{dc} = \frac{c_o RT}{nFc(c_o - c)} \quad (\text{IV-D2}) \]

Based on this equation, the largest value of \( dE/dc \) is obtained for \( c = c_o/2 \) or equivalently at \( E = E^0 \). Hence, over a small range potentials around \( E = E^0 \), \( \Delta E = (4RT/nFc_o) \Delta c \).
LIST OF SYMBOLS

\[a\] 0.51023

\[A\] amplitude of time-varying concentration, \(\text{mol/cm}^3\)

\[B_n\] coefficients of Sturm-Liouville system

\[c_o\] bulk concentration of reactant, \(\text{mol/cm}^3\)

\[c\] local concentration of product, \(\text{mol/cm}^3\)

\[\bar{c}\] steady-state concentration of product, \(\text{mol/cm}^3\)

\[\tilde{c}\] time-varying concentration of product, \(\text{mol/cm}^3\)

\[D\] diffusion coefficient, \(\text{cm}^2/\text{s}\)

\[E\] electrode potential, \(\text{V}\)

\[E^\circ\] standard electrode potential, \(\text{V}\)

\[\bar{E}\] steady-state electrode potential, \(\text{V}\)

\[\tilde{E}\] time-varying electrode potential, \(\text{V}\)

\[F\] Faraday's constant, \(9.6485 \times 10^4 \text{ C/mol}\)

\[I\] light intensity

\[\bar{I}\] steady-state light intensity

\[I^*\] amplitude of the time-varying light intensity

\[j\] \(\sqrt{-1}\)

\[k\] \(\ln 10=2.3026\)

\[K\] \(\omega \nu (3D/\alpha v)^{2/3}/\Omega D\), dimensionless frequency

\[n\] number of electrons transferred in redox process

\[r\] reflection loss at the disk electrode surface

\[R\] molar gas constant, \(8.3144 \text{ J/mol K}\)
\( t \) time, s
\( t^* \) \( D_t, \text{cm}^2 \)
\( T \) temperature, K
\( y \) normal distance from the disk electrode, cm
\( Z_n \) eigenfunctions of Sturm-Liouville system
\( \gamma \) \((\Omega/\nu)^{1/2}(a\nu/3D)^{-1/3}\), conversion factor from \( y \) to \( \zeta \)
\( \Gamma \) gamma function
\( \varepsilon \) extinction coefficient, \( \text{cm}^2/\text{mol} \)
\( \zeta \) \((\Omega/\nu)^{1/2}(a\nu/3D)^{1/3}y\), dimensionless axial distance from the disk electrode
\( \Theta \) \( t\Omega D(a\nu/3D)^{2/3}/\nu\), dimensionless time,
\( \Theta \) dimensionless concentration
\( \lambda \) wavelength, nm
\( \lambda_n \) eigenvalues of Sturm-Liouville system
\( \nu \) kinematic viscosity, \( \text{cm}^2/\text{s} \)
\[ \rho \left( \frac{1}{r(\lambda, E)} \right) \frac{\partial r(\lambda, E)}{\partial E} \bigg|_{\epsilon = \epsilon^*} \] electromodulation reflection coefficient, \( \text{V}^{-1} \)
\( \phi \) phase shift of the time-varying optical signal with respect to original perturbation signal
\( \psi \) dimensionless function defined in Eq. IV-8
\( \omega \) potential modulating frequency, rad/s
\( \omega^* \) \( \omega / D \), rad/cm\(^2\)
\( \Omega \)  
rotation rate of the disk electrode, rad/s

**Suffixes**

- **ac**  
oscillatory
- **dc**  
steady-state
- **L**  
evaluated at the bottom of the electrochemical cell \((y=L)\)
- **ss**  
steady-state
- **t**  
 transient
- **0**  
evaluated at the disk electrode surface \((y = 0)\)

**REFERENCES**


CHAPTER V

POTENTIAL MODULATION NORMAL INCIDENCE
REFLECTION ABSORPTION UV-VISIBLE SPECTROSCOPY
UNDER FORCED CONVECTION: EXPERIMENTAL ASPECTS*

V-1. INTRODUCTION

A theoretical treatment was presented in the last chapter for the quantitative analysis of potential modulation normal incidence reflection absorption UV-visible spectra of solution phase, optically absorbing species produced at the surface of a rotating disk electrode (RDE).\textsuperscript{1} This technique is based on measurements of the modulation in the absorptivity of the solution (along the axis of rotation of the RDE) generated by the application of a sinusoidal voltage of small amplitude to the RDE polarized at a potential at which the electroactive species present in the (bulk) solution is reduced or oxidized. As shown by the theory, the ratio $(I^*/I_{dc})$, where $I^*$ is the amplitude of the ac-, and $I_{dc}$ the magnitude of the dc- components of the optical signal, is proportional to the extinction coefficient of the electrogenerated species and to the absolute value of the integral of the time-independent component of the oscillatory dimensionless concentration profile.

\* This chapter is in press:
M. Zhao and D. A. Scherson, \textit{J. Electrochem. Soc.}

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This chapter describes various experimental aspects of the methodology and presents data for the oxidation of \([\text{Fe(CN)}_6]^{4-}\) in aqueous solutions. The results obtained have made it possible to verify the predictions made by the theory, including the dependence of the magnitude of the signal on the rotation rate of the electrode and on the frequency of the potential perturbation. In addition, excellent quantitative agreement was found between the spectra as evaluated from the \(I^*/I_{dc}\) data, and that obtained by conventional means \textit{without introducing any adjustable parameters}.

V-2. EXPERIMENTAL

A schematic diagram of the optical set-up for potential modulation (near) normal incidence reflection absorption UV-visible spectroscopy measurements at a rotating disk electrode (RDE) is shown in Figure V-1. The spectrometer consists of an ultra-stable arc Xenon lamp (USA 150-3, Optical Radiation Corp.) mounted on an Oriel housing (Model 6136), and a Jobin-Yvon concave holographic grating monochromator (Model H-10) driven by a computer-controlled stepper motor. The monochromatic light is first collimated with a convex lens (\(L_1; f = 15\, \text{cm}\)) and then reflected off a flat mirror (M1) to direct the beam (vertically) along the axis of rotation of the RDE. As is the case with the arrangement for magnetic circular dichroism measurements,\(^2\) all these components are installed on an optical rail which rests in this case on the leg braces of a heavy table.
Figure V-1. Schematic diagram of optical set-up for potential modulation (near) normal incidence reflection absorption UV-visible spectroscopy measurements at a rotating disk electrode (RDE).
The collimated beam (ca. 1 x 2.5 mm) is focused on the RDE surface with a large lens (L2; f = 25 cm) placed above the table directly below the cell. After reflection, the beam is redirected along the plane of the table by means of another flat mirror (M2) and focused onto the photomultiplier detector (Hamamatsu R712) with an additional lens (L3).

The magnitude of the ac signal was determined using a lock-in amplifier (Stanford Research Systems, Model SR-510) by adjusting the phase until the observed value was maximized. The time constant was set at 10 s, and a period of 60 s was allowed before collecting an average of 60-80 readings for each individual measurement. A voltage proportional to $I_{dc}$ (the dc light intensity level) was measured from the output of the photomultiplier preamplifier and digitized using the a/d converter of the SR-510. Both $I^*$ and $I_{dc}$ were stored in the computer for further processing.

All measurements were carried out at a near normal incidence angle using a all-quartz electrochemical cell, consisting of a cylinder fused to a flat optical window, and a Pine rotator/rotating ring-disk electrode (RRDE) system. Data were acquired for both a Au/Au and a Pt/Pt RRDE (Disk area: 0.164 cm²) using a PAR 173 potentiostat. A gold foil (2.4 cm²) and a Ag/AgCl (Re-5, BAS, West Lafayette, IN) were used as counter and reference electrodes, respectively. Since only the response of the disk was of interest here, the ring was always kept disconnected. However, it would be possible to complement measurements of the type described in this work by monitoring at the ring electroactive species.
generated at the disk without altering the assumptions upon which the optical-hydrodynamic-electrochemical theory is based.

Experiments were performed in \( \text{K}_4\text{Fe(CN)}_6/0.5 \text{ M K}_2\text{SO}_4 \) aqueous solutions at room temperature using \( \text{K}_4\text{Fe(CN)}_6\cdot3\text{H}_2\text{O} \) (Aldrich, reagent grade) and \( \text{K}_2\text{SO}_4 \) (Baker Analyzed reagent) as received. Solutions of the iron complex salt were prepared by dissolving the desired amount of the material in solid form into \textit{deareated} \( \text{K}_2\text{SO}_4 \) solutions. This procedure made it possible to greatly diminish the extent of oxidation of the ferrous complex.

Measurements aimed at monitoring the dependence of the optical response on the frequency of the potential perturbation (\( \omega \)) and on the rotation rate of the disk (\( \Omega \)) were conducted by polarizing the electrode at the potential observed for an equimolar solution of \( \text{Fe(CN)}_6^{3-}/\text{Fe(CN)}_6^{4-} \) (0.26 V vs. Ag/AgCl). This potential (except for activity corrections) should correspond to the standard reduction potential of this redox system denoted hereafter as \( E^0 \). The spectrometer was set at 420 nm, a wavelength at which \( \text{Fe(CN)}_6^{3-} \) exhibits an absorption maximum and the absorptivity of \( \text{Fe(CN)}_6^{4-} \) is negligibly small. For the first type of experiments \( \omega \) was varied between 1 and 5 Hz using a constant rotation rate of 160 rpm, whereas for the second type of measurements \( \omega \) was set at 1 Hz and the rotation rate was changed from 90 to 1050 rpm.

Extinction coefficient \( (\varepsilon) \) \( \text{vs.} \) wavelength \( (\lambda) \) curves were determined from the magnitudes of \( I^*/I_{dc} \) obtained at values of \( \lambda \) using \( \omega = 1 \text{ Hz, and } \Omega = 160 \text{ rpm.} \) Unless otherwise specified, the concentration of
the ferrous complex was 10 mM and the amplitude of the potential perturbation (ΔE) was 10 mV.

For measurements in the spectral region where the absorption of the reactant ([Fe(CN)₆]⁴⁻) may not be neglected, i.e. λ < 400 nm, the pathlength must be decreased so that the absorptivity mostly due to [Fe(CN)₆]⁴⁻ will be well below total light extinction. As shown in Figure V-2, the quartz window was mounted on the bottom of the cell forming a recess. This strategy enabled measurements to be performed with a large amount of electrolyte so that the actual concentrations of the reactant and product may be assumed to remain constant throughout the run.

For these experiments, the gold RDE was placed about 5 to 6 mm away from the quartz window. No differences in the values of the diffusion limiting currents could be found as the gap was increased indicating that despite the close proximity of the window the system indeed complies with the expected hydrodynamic behavior of a conventional RDE arrangement. Measurements were performed in 3 and 10 mM solutions of [Fe(CN)₆]⁴⁻ in 0.5 M K₂SO₄ using a modulation frequency of 1 Hz, amplitude of 10 mV about the standard redox potential for this redox couple and a rotation rate of 160 rpm.

V-3. RESULTS AND DISCUSSION

Based on the analysis presented in Chapter IV, which assumes that
Figure V-2. Schematic diagram of the cell with short pathlength and large volume.
the kinetics for the heterogeneous electron transfer reaction are fast (so that the applied potential prescribes the relative ratio of the surface concentrations of the oxidized and reduced species), the largest variation in the concentration of the reactant (or product) at the electrode surface $c(0, t)$ is obtained when $c = c_o/2$ where $c_o$ is the bulk concentration of the reactant. Such condition is achieved when $E = E^\circ$. Figure V-3 compares the magnitude of $I^*/I_{dc}$ as a function of $(E - E^\circ)$ predicted by the theory (solid line) with that observed experimentally (circles) using $\Omega = 160$ rpm, $\omega = 1$ Hz via the equation

$$I^*/I_{dc} = 2e(\lambda) kA *(\nu/\Omega)^{1/2}(3D/\alpha\nu)^{1/3}\int_0^\infty \Psi d\zeta$$

(V-1)

where $e(\lambda = 420 \text{ nm}) = 1.14 \times 10^{-6} \text{ cm}^2/\text{mol}$, $k = 2.303$, $\nu = 0.01 \text{ cm}^2/\text{s}$, $\Omega = 16.8 \text{ rad/s}$ (160 rpm), $D = 7.3 \times 10^{-6} \text{ cm}^2/\text{s}$, $\alpha = 0.51023$ and the integral $\int_0^\infty \Psi d\zeta = 0.29$, evaluated for $K = 13.6$, where $K$ is the dimensionless frequency at the prescribed $\Omega$ and $\omega$. $A^*$ in the equation above is the amplitude of the concentration modulation, which for the redox system under analysis can be obtained directly from the Nernst equation, i.e.

$$A^* = 0.5 c_o \left\{ (1 + \exp(\beta(E^\circ - E + \Delta E))^{-1} - (1 + \exp(\beta(E^\circ - E - \Delta E))^{-1} \right\}$$

where $\beta = nF/RT$ and $E$ is the electrode potential. As judged by the results, the agreement between theory and experiment using $\Delta E = 10 \text{ mV}$, $E^\circ = 0.26 \text{ V}$ vs. Ag/AgCl, $c_o = 10 \text{ mM}$, $n = 1$, $F = 96485 \text{ C/mol}$, $R = 8.314 \text{ J/K\cdot mol}$, $T = 298 \text{ K}$ is quantitative indicating that indeed the highest sensitivity is attained by modulating the potential about $E^\circ$.

Figure V-4 displays data for the dependence of $(I^*/I_{dc})$ on the
Figure V-3. Comparison of the magnitudes of $I^*/I_{dc}$ predicted by the theory (solid line) with that obtained experimentally (circles). $\Omega = 160$ rpm, $\omega = 1$ Hz, $c[Fe(CN)_6^{4-}] = 10$ mM, $\Delta E = 10$ mV (see text for further details).
Figure V-4. Dependence of $I^*/I_{dc}$ on the rotation rate for a range of values between 9.4 and 110.0 rad/s (90 - 1050 rpm) obtained for three independent sets of measurements (circles, triangles and filled squares). $\omega = 1$ Hz, $c[\text{Fe(CN)}_6^{4-}] = 10$ mM, $\Delta E = 10$ mV. The solid line was obtained based on theory.
rotation rate in the range 90 - 1050 rpm obtained for three independent sets of measurements (see circles, triangles and filled squares) for a potential modulation frequency of $\omega = 1$ Hz about (a steady state potential) $E^o$. Despite the slight dispersion, the experimental values were found to cluster around the theoretically predicted curve (solid line) based on Eq. V-2 below and the same parameters specified above.

$$I^*/I_{dc} = \varepsilon(\lambda) k(\Delta EnFC_o/2RT)(\nu/\Omega)^{1/2}(3D/\alpha\nu)^{1/2}\left|\int_0^\infty \Psi d\zeta\right|$$ (V-2)

Similar good agreement was obtained for experiments in which the frequency of the perturbation was varied between 1 - 5 Hz at constant $\Omega$ (= 160 rpm) (see Figure V-5). The values of $I^*/I_{dc}$ in this case were lower than those predicted from Eq. V-2 as $\omega$ was increased. Such discrepancy cannot be attributed to experimental dispersion, as this behavior was consistently observed in every set of independent measurements (see open circles, filled circles, triangles and filled squares).

Perhaps the most remarkable success of the theory is illustrated by the excellent agreement obtained between $\varepsilon(\lambda)$ vs. $\lambda$ calculated based on the magnitude of $I^*/I_{dc}$ observed experimentally, and the value of $\left|\int_0^\infty \Psi d\zeta\right|$ determined by numerical means (see triangles and solid circles in Figure V-6), and the spectrum of Fe(CN)$_6^{3-}$ reported in the literature$^3$ (or measured independently in this laboratory, see solid line in the same Figure) via the equation

$$\varepsilon(\lambda) = \left(\frac{I^*/I_{dc}}{k(\Delta EnFC_o/2RT)(\nu/\Omega)^{1/2}(3D/\alpha\nu)^{1/2}}\left|\int_0^\infty \Psi d\zeta\right|\right)$$ (V-3)
Figure V-5. Dependence of $(I^*/I_{dc})$ on the frequency of the perturbation in the range between 6.3 and 31.4 rad/s (1 - 5 Hz) obtained for three independent sets of measurements (circles, triangles and filled squares). $\Omega = 160$ rpm, $c[\text{Fe(CN)}_6^{4-}] = 10$ mM, $\Delta E = 10$ mV. The solid line was obtained based on theory.
Figure V-6. Comparison between $\varepsilon(\lambda)$ vs. $\lambda$ data obtained by conventional transmission spectroscopy (solid line) and that derived from the magnitude of $I^*/I_{dc}$ determined from potential modulation experiments and the value of $\int_0^\infty \Psi d\zeta$ determined by numerical means for $c_0 = 10$ mM (triangles) and $c_0 = 3$ mM (solid circles). The open squares were obtained in measurements in which the potential was modulated about 0.0 V (see text for details).
using \( c_o = 10 \text{ mM} \) (solid circles) or 3 mM (open triangles) solutions (see Figure V-6) and the same parameter values specified earlier. As expected, \( \varepsilon(\lambda) \) vs. \( \lambda \) is not a function of the concentration of the species in solution, as essentially identical data were obtained for both concentrations. Very similar results (not shown in the figure) were obtained using a Pt ring-disk electrode. Finally, no signal could be detected by modulating the potential at values far removed from \( E^0 \) as illustrated by the results obtained about 0.0 V shown by the open squares in Figure V-6. The spectra in this figure were measured within the wavelength range in which the absorption of the reactant ([Fe(CN)]\(_6\))\(^{4-}\) is negligible.

For the wavelengths shorter than \( ca. 400 \text{ nm} \), a region where both reactant and product absorb light, the situation is complicated due to the different diffusion coefficients of the two species. According to the treatment in Section IV-3.C, expressions needed for the analysis of data of this specific class of systems are given by

\[
\left( \frac{I^*}{I_{dc}} \right) \cos \phi = P_1 \int_0^\infty \text{Re}(\Psi_1) d\zeta + P_2 \int_0^\infty \text{Re}(\Psi_2) d\zeta \tag{V-4}
\]

\[
\left( \frac{I^*}{I_{dc}} \right) \sin \phi = P_1 \int_0^\infty \text{Im}(\Psi_1) d\zeta + P_2 \int_0^\infty \text{Im}(\Psi_2) d\zeta \tag{V-5}
\]

\[
\phi(\lambda) = \arctan \left[ \frac{P_1 \int_0^\infty \text{Im}(\Psi_1) d\zeta + P_2 \int_0^\infty \text{Im}(\Psi_2) d\zeta}{P_1 \int_0^\infty \text{Re}(\Psi_1) d\zeta + P_2 \int_0^\infty \text{Re}(\Psi_2) d\zeta} \right] \tag{V-6}
\]

where \( P_i = 2k\varepsilon_i(\lambda)\gamma_i A_{i*} \).
One of the key issues that must be considered in the planning of this type of experiment is the overall absorptivity due to the reactant as long pathlengths can lead to excessive attenuation of the beam and thus to a large decrease in the light intensity reaching the detector. In fact, under extreme conditions this effect can result in a total loss of signal. This phenomenon is illustrated in Figure V-7 by the results obtained using the long-pathlength (about 8 cm) cell described in Experimental Section (see Figure V-1), where the solid lines were calculated based on Eqs. V-4 - V-6 using extinction coefficients for both the ferro and ferric complexes in the same electrolyte determined in this laboratory by conventional transmission spectroscopy. As can be seen, the value of $I^*/I_{dc}$ observed experimentally drops precipitously for $\lambda < 410$ nm.

Figure V-8 displays the experimental values of $I^*/I_{dc}$ as a function of wavelength for two concentrations of ferrocyanide, 3 mM (triangles) and 10 mM (circles) under identical conditions as those in the long-pathlength experiment (Figure V-7) except that the distance between the electrode and the window was decreased to 6 mm. As indicated, the agreement between theory and experiment is excellent providing further evidence that the results obtained from this method are indeed quantitative even when the absorption due to the reactant is not negligible.
Figure V-7. Plots of $I^*/I_{dc}$ versus wavelength for 10 mM (circles) solutions of ferrocyanide in 0.5 M potassium sulfate. Modulation frequency: 1 Hz. Modulation amplitude: 10 mV. Rotation Rate: 160 rpm. Electrode-window gap: ca. 8 cm. The solid lines were calculated from theory using extinction coefficients for the two redox species in the same electrolyte determined by conventional transmission spectroscopy.
Figure V-8. Plots of $I^*/I_{dc}$ versus wavelength for 3 mM (triangles) and 10 mM (circles) solutions of ferrocyanide in 0.5 M potassium sulfate using the same conditions specified in the caption Figure V-7, except that the electrode-window gap was 6 mm.
The experimental arrangement used for these measurements makes it possible to detect values of \( \frac{I^*}{I_{dc}} \) as low as \( 2 \times 10^{-4} \). An estimate of the equivalent absorptivity \( A \), associated with this parameter can be made by rearranging Eq. V-3 and using the explicit expression for the integrated real concentration profile, i.e. \( \int_0^\infty c dy = 0.5 c_o \delta B \), where \( 0.5 c_o \) is the surface concentration of the reactant (or product), \( \delta = (v/\Omega)^{1/2} (3D/a \nu)^{1/3} \) is the thickness of the diffusion boundary layer and \( B = 0.5055 \) to yield

\[
A = 2e \int_0^\infty c dy = \left( \frac{2BRT}{k\Delta EnF} \right) \left( \int_0^\infty \Psi d\zeta \right) \left( \frac{I^*}{I_{dc}} \right)
\]  

(V-7)

As shown in Chapter IV, the maximum value of the integral in the right hand side of the equation above is about 0.51. Hence, for experiments conducted at room temperature and \( \Delta E = 10 \text{ mV} \) and \( n = 1 \), \( A = 4.4 \times 10^{-4} \). If the extinction coefficient of the product is on the order of \( 10^6 \text{ mol}^{-1}\text{cm}^2 \), the total number of moles per \( \text{cm}^2 \) probed by the beam amounts to \( 4.4 \times 10^{-10} \) and therefore on the order of a single monolayer. This represents an improvement of about one order of magnitude with respect to the dc method described in Chapter II.

REFERENCES


PART TWO

IN SITU REFLECTION ABSORPTION
MAGNETIC CIRCULAR DICHROISM
CHAPTER VI

IN SITU REFLECTION ABSORPTION
MAGNETIC CIRCULAR DICHROISM:
METHODOLOGY AND PRELIMINARY RESULTS*

VI-1. INTRODUCTION

The development of a host of new in situ spectroscopic techniques over the past decade has made a major impact towards achieving a better understanding of elementary processes at electrode-electrolyte interfaces.\(^1\) Because of their high sensitivity, in situ optical methods in the UV-visible region lend themselves to this type of application and, as such, have been widely used for monitoring a variety of surface reactions. These include the adsorption of ions, atoms and molecules on electrode surfaces, as well as the changes in the electronic structure of metals, and particularly single crystal surfaces, induced by the externally applied potential.\(^2\)

Increased sensitivity to changes in the physicochemical properties of the interface may be attained by monitoring modifications in the polarization state of light reflected off electrode surfaces. This is best

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* This chapter has been published:
illustrated by the widespread application of ellipsometric techniques to the general field of electrochemistry. Methods that rely on the analysis of the behavior of right and left circularly polarized light at electrochemical interfaces, however, have received far less attention. This may be attributed in part to the rather restricted class of molecules of electrochemical interest which possess chiral centers. Optical activity can be induced, however, by applying an external magnetic field, a phenomenon that constitutes the basis of a well developed spectroscopic method known as magnetic circular dichroism, MCD. In direct analogy with the more conventional circular dichroism, MCD measures the differences in the absorption coefficient obtained with right and left circularly polarized light of a species either in solution or in the solid state. This technique can provide unique information that can be complementary to that derived from other methods. In particular, the shape and sign of the MCD features may be used to make firm band assignments of electronic transitions, and the differences in the MCD response of otherwise overlapping spectral features enables, in principle, the detection of small bands buried under more prominent features in conventional absorption spectra.

Despite its rather early inception, only a few illustrations of the use of MCD in the ex situ reflection absorption mode have been published in the literature, with most attention being centered on magnetic materials.

This chapter will describe various aspects of the experimental
methodology involved in the acquisition of *in situ* reflection absorption MCD and present preliminary data for the potential modulated MCD response of the basal plane of highly oriented pyrolytic graphite HOPG(bp) in acid electrolytes.

VI-2. EXPERIMENTAL

The instrumental array involved in the *in situ* reflection absorption MCD measurements is shown in Figure VI-1. Right and left circularly polarized light was obtained by passing a laser beam (either a HeNe or Ar*-ion) first through a fixed polarizer (calcite, Glan-Taylor) \( P \), and a Morvue Electronic Systems Model PEM-3 50 kHz photoelastic modulator with an isotropic infrasil fused quartz optical element oriented at 45° with respect to the axis of \( P \). The light was then directed nearly parallel to the axis of an 8T (80,000 Gauss) superconducting magnet, reflected off the electrode surface back through the magnet base and redirected along the optical table to a collecting lens placed in front of a photomultiplier detector, PMT. This geometric arrangement is quasi ideal as the direction of propagation of the light is very close to parallel (< 1.5°) to the applied magnetic field, which leads to a maximization of the MCD effect. Despite the small angle, the sharp reflection from the air-window interface could easily be separated from the more diffuse reflection from the slightly corrugated HOPG(bp) surface, so that only the latter could be directed to the PMT.
Figure VI-1. Schematic diagram of a reflection absorption magnetic circular dichroism experiment.
The electrochemical cell employed in these studies was identical in design to that developed in this laboratory for conventional reflection absorption studies, except that the prism was replaced by a flat optical glass window. The aluminum frame was also modified to enable the cell to be suspended from the top of a liquid helium Dewar so as to place the electrode surface at a point where the magnetic field has the highest homogeneity. A gold wire loop was used as the counter electrode and a saturated calomel electrode, SCE, was employed as the reference, which was connected via a closed stopcock to the main cell compartment through a long Teflon tube. The electrical connections to the cell were made with thin copper wires. The potential of the working electrode was controlled by a Pine potentiostat. All measurements were conducted in the cyclic voltammetric mode at a rate of 200 mV/s while monitoring the current response in a Yokowaga X-Y-Y recorder.

For the acquisition of MCD data, the current output of the PMT was fed directly into the current input of the lock-in amplifier (Stanford Research Instruments, Model SR 510) and demodulated using the reference generated by the control box of the PEM. The lock-in output, which is proportional to the MCD signal, was then fed into a signal averager synchronized with the electrode potential. For this purpose, a potential step signal extracted from the signal generator of the Pine potentiostat associated with each scan direction reversal was used as a trigger. In this fashion curves could be obtained for a signal proportional to the MCD effect as a function of the applied potential, E. After
collection, the MCD vs. potential data were transferred to a computer for further processing.

Experiments were performed for different values of the applied magnetic field at all wavelengths available with the two lasers. For each applied magnetic field and wavelength the electrochemically modulated MCD data was normalized by the MCD signal obtained at an arbitrary reference potential $E_{\text{ref}}$. In analogy with more conventional electroreflectance measurements the data to be presented are displayed in the form of $\Delta R_{\text{MCD}}/R_{\text{MCD(Ref)}}$, where $\Delta R_{\text{MCD}}$ corresponds to the difference in the signal proportional to the MCD effect obtained at an arbitrary potential $E$, $R_{\text{MCD}}(E)$, and that at the reference potential selected, $R_{\text{MCD(Ref)}}$. For these measurements $E_{\text{ref}}$ has been chosen arbitrarily to be either of the two extreme potentials involved in the voltammetric scans e.g. 0.2 or 0.9 V vs. SCE.

Conventional electroreflectance experiments involving HOPG(bp) were obtained using an apparatus and techniques described in Ref. 7.

VI-3. RESULTS AND DISCUSSION

The cyclic voltammetry curves of freshly cleaved HOPG(bp) surface in 0.05 M $\text{H}_2\text{SO}_4$ in the range between 0.2 and 0.9 V vs. SCE were found to be featureless and thus in agreement with those reported elsewhere. To the level of sensitivity of the equipment used, no changes or distortions in the voltammetry curves were observed as the magnetic
field was increased from 0 to ca. 7.8 T. This should not be surprising, as the effects of externally applied magnetic fields on the energetics and kinetics of chemical (and electrochemical) reactions are expected to be very small.\(^8\)

No changes in \(\Delta R_{\text{MCD}}/R_{\text{MCD}}(0.9 \text{ V})\) as a function of the applied potential, \(E\), were found at zero applied magnetic field \((H = 0)\) and \(\lambda = 514.5\) nm (see Curve A, Figure VI-2). As shown in curves B and C in the same figure, however, strongly potential correlated signals could be clearly detected for \(H > 0\) after coaddition of 100 potential cycles. Also noteworthy is the fact that at a given potential the magnitude of the effect increased, albeit not linearly, with the strength of the magnetic field.

Three additional observations provide rather conclusive evidence that the effect observed indeed arises from a modulation in the MCD properties of the cell (including the HOPG(bp), the window and the electrolyte) induced by the applied potential:

(i) the overall effect disappeared when the photoelastic modulator was turned off, or when the light was blocked, and

(ii) a reversal of the direction of the magnetic field led to a corresponding reversal of the sign of the signal observed, as illustrated for the case of \(H = 7.8\) T at a wavelength of 623.8 nm in Figure VI-3.

Except for the magnitude, the sign as well as the increase in \(\Delta R_{\text{MCD}}/R_{\text{MCD}}(0.2 \text{ V})\) as the potential was shifted towards more positive values were found to be same for all the wavelengths examined.
Figure VI-2. Normalized potential modulated reflection absorption MCD signals, $\Delta R_{MCD}/R_{MCD}(0.9 \, \text{V})$ for the basal plane of highly ordered pyrolytic graphite in 0.05 M H$_2$SO$_4$, in the absence (Curve A) and in the presence of an externally applied magnetic field of 4.7 T and 7.8 T (see Curves B and C). Wavelength: 514.5 nm.
Figure VI-3. Plots of the potential modulated, demodulated response of the lock-in amplifier induced by changing the direction of the externally applied magnetic field. Wavelength: 623.8 nm.
According to classical optics, the sense of rotation of circularly polarized light reverses upon reflection. Therefore if a perfect mirror is placed behind a cell containing a given material, any circular dichroism effect will cancel out. For MCD measurements, however, the phenomena actually doubles because the direction of propagation of the light with respect to the magnetic field flips between parallel and antiparallel before and after the reflection. It thus follows that modulations in the reflectivity of the electrode induced by changes in the applied potential will also introduce changes in the MCD associated with the window or the electrolyte. In order to gain insight into this issue and determine whether the potential modulated signal could be ascribed to a surface phenomenon, the intrinsic electroreflectance properties of HOPG(bp) in this energy region were measured using an instrument developed specifically for these purposes. For these experiments, a much larger angle of incidence was employed so as to increase the sensitivity. As indicated in Figure VI-4, the changes in reflectivity (if present) observed for potentials between 0.2 V and 0.9 V in the visible region did not exceed 0.02 %. Unfortunately, the signal to noise ratio for similar experiments in which the intrinsic electroreflectance effect was measured in the presence of the magnetic field with the PEM off (at near normal incidence) was much poorer. Nevertheless, the effect under these conditions was not larger than 0.2 %.

One possible cause for the modulation in the MCD signal induced by the applied potential may be found in changes in the electronic
Figure VI-4. Electoreflectance curve of bare HOPG(bp) measured at 640 nm at an angle of incidence of 50° in 0.05 M H₂SO₄.
structure of HOPG(bp) engendered by the application the external magnetic field. Quantum mechanics predicts that the interaction between a magnetic field applied normal to a two-dimensional electron gas gives rise to a quantization of the electronic energy levels.\textsuperscript{10} The further introduction of a two-dimensional periodic lattice to such two-dimensional electron gas, (a structure that would resemble that of the basal plane of HOPG) has been shown to bring about unique changes in the band structure.\textsuperscript{11} It is thus conceivable that the effect observed may be related to transitions between these levels for which their occupancy will be determined by the externally applied potential, and thus in direct analogy to the shift in the transition energy of surface states induced by the applied potential.\textsuperscript{2}

Further insight into these issues is expected to be gained from more detailed studies which would include measurements with a conventional light source and a monochromator.

From an overall perspective, \textit{in situ} reflection absorption MCD may become a very valuable and indeed highly sensitive probe of the electronic properties of not only bare surfaces, but also of adsorbed species on electrode surfaces as well. Aside from the need for a high field magnet, the equipment required is the same as that involved in more conventional circular dichroism measurements. In fact, sensitivities on the order of $1 \cdot 10^{-7}$ $\Delta A$ units have been recently achieved for MCD experiments in the transmission mode,\textsuperscript{12} which would, in principle, be sufficient to detect signals associated with submonolayer quantities of
moderate to strong MCD active species.

REFERENCES


2. D. M. Kolb in Ref. 1, pp. 87-188.


CHAPTER VII

EXPERIMENTAL ARRANGEMENT FOR IN SITU
MAGNETIC CIRCULAR DICHROISM MEASUREMENTS
OF ELECTROGENERATED SPECIES IN SOLUTION PHASE*

VII-1. INTRODUCTION

Despite the wealth of information magnetic circular dichroism (MCD) can provide regarding the electronic structure of molecules and solid state materials,\textsuperscript{1} the application of this technique to the study of systems of electrochemical interest has received surprisingly little attention.\textsuperscript{2,3} The only illustration of the use of MCD to examine in situ the spectral properties of an electrogenerated species appears to be that of Kobayashi and Nishiyama,\textsuperscript{2} who used a minigrid-electrode spectroelectrochemical cell placed in the strong magnetic field to record transmission MCD spectra of iron(II) and cobalt(I) 4,4',4'',4'''-tetracarboxy-phthalocyanine, TCPC, in aqueous electrolytes.

This chapter describes an alternate experimental arrangement for the acquisition of MCD spectra of electrogenerated species, in which a

\* This chapter has been published:
highly focused beam of light, (aligned almost parallel to the magnetic field), is reflected off the surface of a highly polished solid working electrode at near normal incidence, using a thin layer cell configuration very similar to that developed for reflection absorption infrared spectroscopic studies. This specific geometry makes it possible to essentially cancel the contributions due to natural circular dichroism while doubling the MCD signal. Highly detailed MCD spectra were collected in the region between 575 and 700 nm for Co(II) \(4,4',4'',4''''\)-tetrarsulphonate phthalocyanine, Co(II)TsPc and the (electrochemically generated) Co(III)TsPc derivative in aqueous 0.05 M \(\text{H}_2\text{SO}_4\). The MCD spectra of the latter (oxidized) species was found to be very similar to that reported by Stillman and coworkers for the axially coordinated dicyanide-Co(III)-phthalocyanine, Co(III)Pc(CN)$_2$, in non-aqueous electrolytes (4).

VII-2. EXPERIMENTAL

Many of the components of the MCD instrument used for the measurements reported in this chapter, including the superconducting magnet, have been described in Chapter VI. A schematic diagram of the experimental set-up is shown in Figure VII-1. The spectrometer consists of a tungsten-halogen lamp mounted in an Oriel housing and a Jobin-Yvon concave holographic grating monochromator (Model H-10) driven by a computer (IBM XT) - controlled stepper motor. The monochromatic
Figure VII-1. Schematic diagram of the instrument for MCD measurements of electrogenerated species in solution phase.
light is collimated with a convex lens and reflected off a flat mirror to
direct the beam along the bore of the superconducting magnet. Right- and
left-circularly polarized light are produced in an alternate fashion (50.3
kHz) by passing the collimated light first through a fixed polarizer and
then through a photoelastic modulator (PEM-3, Morvue). The retardation
(at each specific wavelength) is adjusted automatically by the computer
via a D/A board. All these components are installed on an optical rail
which is attached in turn to the optical table by means of an aluminum
bracket.

The collimated (ca. 3mm diameter), modulated beam is focused on
the electrode surface with a large lens placed on the optical table directly
below the magnet. After reflection, the beam is redirected along the plane
of the table by means of another flat mirror and focused onto the
photomultiplier detector with an additional lens.\textsuperscript{5}

The electronic signal processing was largely based on the method
described by Policke et al.\textsuperscript{6} to yield both the conventional absorption
spectra and a signal proportional to the MCD spectra simultaneously,
using a Stanford SR510 lock-in amplifier.

The electrochemical cell, shown in Figure VII-1, consists of a coin-
shaped gold working electrode (ca. 1.9 cm diameter) cast in Kel-F, and a
flat, circular quartz window placed parallel to the electrode surface. The
gap between the electrode and the window can be adjusted with a Teflon
rod attached to the Kel-F piece, which slides into a hole drilled in the
main body of the all-Teflon cell. The cell is assembled using an all-
aluminum frame by compressing an O-ring inteposed between the window and the main-body of the cell as indicated in the figure. Electrolyte can be delivered and removed from the cell using two Teflon tubes press-fit into two separate holes drilled in the main body of the cell. During the electrochemical experiments one of the tubes is used as a Luggin capillary to connect to a saturated calomel reference electrode (SCE) placed outside the magnet. The cell is suspended inside the bore of the superconducting magnet at the correct height by means of a long plastic bar attached to the aluminum frame.

Co(II)TsPc was synthesized and purified by the method of Weber and Busch\(^7\) and characterized by UV-visible spectroscopy.

MCD spectra in the region between 500 and 700 nm were first recorded for the neat 0.05 M H\(_2\)SO\(_4\) solution at 0.3 and 1.3 V vs. SCE, i.e. in the double layer and oxide regions with the magnet at 7.7 T. Subsequently, the electrolyte was replaced by a 10\(^{-4}\) M CoTsPc in 0.05 M H\(_2\)SO\(_4\) solution and spectra were acquired with the electrode polarized at 0.0 V vs. SCE, at which the macrocycle is in the Co(II) (or reduced) state and then at a potential positive enough for the species to be predominantly in Co(III) (or oxidized) state, i.e. 0.6 V vs. SCE. About 20 min. were allowed to elapse, after each potential change, in order for the electrolysis to reach completion. Based on the experimentally determined absorbance for the Co(II)TsPc obtained during the MCD measurements, and the extinction coefficient measured in independent experiments (involving a conventional UV-visible spectrometer) the solution gap was estimated to
be on the order of 0.1 mm.

For some of the measurements involving neat 0.05 M H$_2$SO$_4$ solutions the wavelength of the incident radiation was fixed at a few values within the range between 500 and 700 nm and the MCD response examined while scanning the potential in a linear fashion at 300 mV/s using a signal averager to increase the signal-to-noise ratio.

Unless otherwise stated all the MCD data presented in this chapter are displayed in the form of $\Delta \varepsilon_M$ (dm$^3$·mol$^{-1}$·cm$^{-1}$·T$^{-1}$) versus wavelength, where $\Delta \varepsilon_M = \Delta A / c l H$, in which $\Delta A$ is the absorbance difference between left-, and right-circularly polarized light, $c$ the concentration in mol·dm$^{-3}$, $l$ the pathlength in cm, and $H$ the magnetic field strength in T.

VII-3. RESULTS AND DISCUSSION

Consider an electrode which is not MCD active at any potential. If the reflectivity of such an electrode is modified by changes in the applied potential, due, for example, to interfacial charging or ionic adsorption, a potential varying MCD signal would be observed if any of the materials in the path of the beam (within the magnetic field) is MCD active. These would include the window and the electrolyte. Gold (and few other electrode materials as well) affords an ideal means of exploring the extent to which these (artifactual) effects may affect the MCD spectra of the species under study, since the electrochemical formation of
the oxide brings about a large change in the surface reflectivity of bare gold without altering the solution composition. To this end, a series of experiments were conducted in neat 0.05 M H₂SO₄, in which the MCD signals were monitored at various wavelengths as the potential was varied in a linear fashion in a region encompassing oxide formation (and reduction). For all wavelengths examined, the MCD signals were found to exhibit no dependence on the applied potential indicating that the contributions arising from reflectivity modulation (under the condition in which these experiments were performed) are indeed negligible. This is shown in Figure VII-2 for measurements performed at 600 nm in which the current recorded during a linear potential scan at 100 mV/s (Curve A), the normalized reflectance ΔR/R (obtained at an incident angle of 70°) (Curve B) and the normalized MCD signal given as ΔR_{ac}/R_{ac} (Curve C) are displayed as a function of the applied potential. ΔR_{ac} is the reflectivity difference between left- and right-circularly polarized light.

In a separate set of measurements, MCD signals were recorded in the wavelength region of interest with the electrode polarized at 0.3 V and at 1.3 V. In both cases, the curves obtained were found to be very similar displaying a monotonic decrease in R_{ac}/R_{dc} towards higher energies.

A very different MCD spectral behavior was observed upon introducing the 10⁻⁴ M Co(II)TsPc/0.05 M H₂SO₄ solution. Figure VII-3A shows Δε_M vs. wavelength curves with the electrode polarized at a
Figure VII-2. A. Cyclic voltammetry obtained in a linear scan in the positive direction between 0.3 and 1.3 V vs. SCE for a polycrystalline gold electrode in 0.05 M H$_2$SO$_4$ aqueous solutions. Electrode Area: 2.85 cm$^2$.

B. Normalized reflectivity change of polycrystalline gold obtained in 0.1 M HClO$_4$ at 600 nm with p-light. The measurements were conducted at an angle of incidence of 70°.

C. Normalized reflectivity differences for left-, and right-circularly polarized light for the same electrode and conditions described in A at a near normal incidence angle. Magnetic Field Strength, $H = 7.7$ T.
Figure VII-3. In situ MCD (top) and conventional absorption spectra (bottom) of Co(II)TsPc in 0.05 M H$_2$SO$_4$ aqueous electrolyte. $H = 7.7$ T (other experimental conditions are specified in the text).
potential at which the macrocycle is predominantly in the reduced state, normalized by the MCD spectrum obtained in the same spectral region at 0.3 V in the absence of CoTsPc in solution. In agreement with results reported in the literature, the conventional absorption spectra recorded during the MCD data acquisition (see Figure VII-3B) showed a well-defined band at 625 nm with a shoulder at a slightly lower energy (see Table VII-I). In analogy with the assignment proposed in the case of Co(II)Pc, Co(II)crown Pc and Co(II)TCPC in solution phase, the features observed both in the conventional absorption and MCD spectra (see Table VII-I) are attributed to the characteristic Q-band associated with the phthalocyanine-ring $\pi-\pi^*$ transition ($^1A_{1g} \rightarrow ^1E_u$).

Significant changes in the spectra were observed when the electrode was polarized at a potential positive enough for the complete oxidation of the macrocycle to ensue (see Figure VII-4 and Table VII-I). The absorption spectra in this case displayed a prominent Q-band at about 668 nm with a small vibrational feature at higher energy. The corresponding MCD spectra for this oxidized species is remarkably similar to those reported by Stillman and co-workers for the di-axially coordinated CoPc(CN)$_2$ in dimethyl sulfoxide solutions. As indicated by these authors, the spectra of these species are characterized by derivative-shaped curves associated with A terms. According to theory these terms can be observed for species that possess at least a three-fold symmetry axis and could thus display a degenerate excited state. Hence, in the presence of the magnetic field the degeneracy would be lifted giving rise
Table VII-I. Comparison between the *In Situ* Absorption Spectra and Magnetic Circular Dichroism Spectra of Co\textsuperscript{II}TsPc and Co\textsuperscript{III}TsPc Obtained in This Work and Other Closely Related Compounds \(^a\)

<table>
<thead>
<tr>
<th>species</th>
<th>absorption spectra</th>
<th>MCD spectra</th>
<th>ref</th>
</tr>
</thead>
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<tr>
<td></td>
<td>peak position(^b)</td>
<td>FWHM(^c)</td>
<td>+</td>
</tr>
<tr>
<td>Co\textsuperscript{II}TsPc</td>
<td>625 (658)</td>
<td>73</td>
<td>613</td>
</tr>
<tr>
<td>Co\textsuperscript{II}TsPc</td>
<td>623 (653)</td>
<td>76</td>
<td></td>
</tr>
<tr>
<td>Co\textsuperscript{II}TCPc</td>
<td>625 (677)</td>
<td>105</td>
<td>606</td>
</tr>
<tr>
<td>Co\textsuperscript{III}TsPc</td>
<td>668 (605)</td>
<td>32</td>
<td>602 658</td>
</tr>
<tr>
<td>Co\textsuperscript{III}TsPc</td>
<td>668 (604)</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td>Co\textsuperscript{III}PC (CN)(_2)</td>
<td>672 (605)</td>
<td>35</td>
<td>604 663</td>
</tr>
</tbody>
</table>

\(^a\) The energy of all spectral features are given in nanometers.
\(^b\) The number in parentheses gives the position of the observed shoulder.
\(^c\) Full width at half-maximum.
Figure VII-4. *In situ* MCD (top) and conventional absorption spectra (bottom) of Co(III)TsPc in 0.05 M H₂SO₄ aqueous electrolyte. $H = 7.7$ T (other experimental condition are specified in the text).
to transitions (at different energies) that would be selectively excited by right and left-circularly polarized light.

The specific technique presented in this chapter could be used for studies involving a general class of electrogenerated species in both aqueous and non-aqueous solvents. In addition it could be directly employed for investigating the electronic properties of species adsorbed on electrode surfaces.

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PART THREE

IN SITU FOURIER TRANSFORM INFRARED
REFLECTION ABSORPTION SPECTROSCOPY
CHAPTER VIII

IN SITU INFRARED STUDIES OF THE Cd-UPD MEDIATED REDUCTION OF NITRATE ON GOLD*

VIII-1. INTRODUCTION

Underpotential-deposited cadmium on Ag, Au and Pt has been found to exhibit electrocatalytic properties for the reduction of nitrate in aqueous media.\textsuperscript{1,2} Insight into the mechanism associated with this process has been recently obtained from experiments involving rotating ring-disk electrodes.\textsuperscript{2} An unambiguous identification of reaction products, however, requires the use of \textit{in situ} methods with molecular and atomic specificity, an area that has experienced extraordinary process in recent years.\textsuperscript{3} Particularly relevant to the study of the electrochemical properties of simple nitrogen containing compounds is the work of Bruckenstein and co-workers who pioneered the use of on-line mass spectrometric techniques for the detection and identification of gas phase products.\textsuperscript{4,5}

One of the main objectives of this work is to elucidate the mechanistic pathways associated with the reduction of nitrate on Au

* This chapter has been published:
mediated by Cd-UPD by using in situ Fourier Transform Infrared Reflection Absorption Spectroscopy, FTIRRAS, for monitoring solution phase species. As will be shown, the results obtained have provided evidence that for \([H^+] < [NO_3^-]\) the electrocatalytic process yields nitrite as the only detectable product. At least two well-defined isosbestic points could be identified in plots of potential difference spectra as a function of the applied potential. This indicates that to the level of sensitivity of \emph{in situ} FTIRRAS the nitrate/nitrite conversion is quantitative. Additional evidence in support of this view was provided by the fact that the magnitude of the ratio of the integrated absorption bands of nitrate and nitrite was found to be constant over a wide potential region.

VIII-2. EXPERIMENTAL

All measurements were carried out using a spectroelectrochemical cell with a 60° beveled CaF₂ prism described in Ref. 6. The FTIR spectrometer and electrochemical equipment have been specified in references 6 and 7. Solutions of HClO₄ (Ultrax, Baker), NaClO₄ (Baker), NaNO₃ (Fisher) and Cd(ClO₄)₂ (Alfa) were made with ultra purified water obtained from a modified Gilmont distillation system. Potentials were measured versus a saturated calomel electrode, SCE. The area of the ellipsoidal, Kel-F cast polycrystalline gold electrode was 1.4cm². All solutions were degassed by bubbling nitrogen (Air Products, 3N).
The p-polarized FTIR-RAS spectra are displayed in the form of 
-ΔR/R versus wavenumber plots, where 

\[-ΔR/R = \frac{-[R(E_{sample}) - R(E_{ref})]}{R(E_{ref})} \]

R(E_{sample}) and R(E_{ref}) represent (unless specified otherwise) the 
coaddition of 1000 interferometric scans with a resolution of 8 cm\(^{-1}\) at a 
given potential E_{sample} and at the reference potential E_{ref}. After recording 
R(E_{ref}), the potential was stepped in sequence to five different values. 
After each potential step, the current was allowed to decrease to a 
negligible level before the acquisition of the spectrum was initiated. The 
spectrum of perchlorate ion involved in the data analysis (see below) was 
recorded by the ion migration method described by Bae et al.\(^8\) These 
calculations were performed by using routines available in the IBM-98 
FTIR computer system.

VIII-3. RESULTS AND DISCUSSION

The cyclic voltammogram of a polycrystalline gold electrode in a 
N\(_2\)-purged 1 mM HClO\(_4\), 0.5 M NaClO\(_4\), 10 mM NaNO\(_3\) solution before 
adding Cd(ClO\(_4\))\(_2\) to a concentration of 3 mM are given in Curves A and 
B, Figure VIII-1. These curves were obtained in the 
spectroelectrochemical cell with the electrode pulled away from the 
optical window. Scans involving a potential region sufficiently wide to 
embrace the oxide region yielded, in the absence of cadmium in the 
solution, curves believed to be characteristic of clean polycrystalline gold 
surfaces. In agreement with Ref. 1, the presence of Cd-UPD (see Curve
Figure VIII-1. Cyclic voltammetry of polycrystalline gold in a N₂-purged 1 mM HClO₄ and 10 mM NaNO₃ before (Curve A) and after (Curve B) adding Cd(ClO₄)₂ to a concentration of 3 mM. These curves were obtained in the spectrobelectrochemical cell with the electrode pulled away from the window. Scan rate: 100mV s⁻¹. Electrode area: 1.4 cm².
B, Figure VIII-1) gives rise to a sizable increase in the current with an onset at about -0.25V vs. SCE which has been attributed to the reduction of nitrate. The pseudo-capacitive current at potential between 0.1 V and the onset of NO₃⁻ reduction is due to Cd-UPD. The electrode was then polarized at +0.40 V vs. SCE, pushed against the window and a reference FTIR spectrum recorded.

The potential difference FTIRRAS spectra obtained at five different potentials according to the method described in the Section VIII-2 are displayed in Figure VIII-2. As clearly indicated, the spectra obtained at -0.30 V and more negative potentials show a negative-going and a positive-going peak centered at 1385 and 1245 cm⁻¹, respectively. These are in accordance with those associated with nitrate and nitrite, respectively. With the exception of the water-related features in the region between 1600 and 1800 cm⁻¹ and the band corresponding to perchlorate at 1120 cm⁻¹ no other peaks could be observed at wavenumbers up to 3000 cm⁻¹ (see Figure VIII-3). As has been discussed in Ref. 8, the decrease in the concentration of solution phase perchlorate is caused by the depletion of solution phase cadmium ions and protons in the thin layer due to the reduction reaction so as to satisfy the electroneutrality condition therein. A more quantitative account of the size of the perchlorate band requires a detailed analysis of ionic migration which includes large contributions from Na⁺. After the spectrum at -0.7 V had been recorded the potential was stepped to 0.4 V and a new spectrum collected (not shown in the figure). The only change observed in this case
Figure VIII-2. Potential difference FTIR-RAS spectra obtained at the indicated potentials using as a reference the spectra collected at +0.4 V vs. SCE recorded prior to polarizing the electrode at potentials sufficiently negative to reduce nitrate. (A) -0.3, (B) -0.4, (C) -0.5, (D) -0.6, (E) -0.7 V vs. SCE.
Figure VIII-3. Potential difference FTIRRAS spectra obtained at -0.4 (A) and -0.7 V (B) vs. SCE in an extended energy region using as a reference the spectrum collected at +0.4 V vs. SCE recorded prior to polarizing the electrode at potentials sufficiently negative to reduce nitrate.
was a decrease in the intensity of the perchlorate band induced by the stripping of the Cd-UPD layer and to a lesser extent by the diffusion of ClO$_4^-$ due to the different activities inside and outside the thin layer. Effects associated with double layer charging are not expected to be significant as the potential of zero charge for polycrystalline Au (for solutions devoid of ions that can undergo specific absorption) is about 0.0 V vs. SCE.$^{10}$

Essentially an identical series of spectra, albeit with the sign reversed, were obtained upon oxidizing the electrochemically generated nitrite immediately following acquisition of the spectral series in Figure VIII-2. The onset potential required for the process was 0.6 V.

On the basis of these results, it may be concluded that in the media selected for these experiments nitrate undergoes reduction to generate nitrite as the only IR detectable product. This behavior is analogous to the solid state reaction of metallic cadmium with nitrate salts which yields in addition to CdO the corresponding nitrite as a product.$^{11}$

Additional information could be obtained by subtracting from each of the potential difference spectra in Figure VIII-2 the contributions from the perchlorate band. This was effected by first collecting a spectrum of perchlorate ion in the absence of Cd and nitrate in the electrolyte and then adding that to each of the spectra in Figure VII-2 a ClO$_4^-$ band of an adequate sign and magnitude to yield a flat background. These perchlorate corrected spectra are shown in Figure VIII-4. As may be seen these curves
Figure VIII-4. Solution-phase perchlorate corrected spectra in Figure VIII-2, according to the method described in the text.
display two well-defined isosbestic points at 1461 and 1321 cm\(^{-1}\) A possible third isosbestic point at about 1160 cm\(^{-1}\) could not be identified due to the much poorer signal to noise ratio in this spectral region. This affords evidence that the nitrate-nitrite conversion is quantitative. Further support of this view is provided by the essentially constant value obtained upon taking the ratio of the integrated bands associated with nitrite and nitrate at each individual potential for which the value determined was 1.0 ± 0.2 (see Figure VIII-5).

In summary, the in situ FTIRRAS measurements have indicated that the electrochemical reduction of nitrate on polycrystalline gold mediated by underpotential-deposited cadmium yields nitrite as the only detectable product in acid media. This conclusion is in accordance with that made on the basis of rotating ring-disk measurements reported in the literature.

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Figure VIII-5. Area of the integrated bands for nitrite, $\text{Area}_{\text{nitrite}}$ versus $\text{Area}_{\text{nitrate}}$ obtained at different potentials. The calculated value for the slope was $1.0 \pm 0.2$. 


CHAPTER IX

IN SITU POTENTIAL DIFFERENCE FTIRAS STUDIES
OF THE ELECTROCHEMICAL OXIDATION
OF ADSORBED CARBON MONOXIDE
ON NICKEL IN ALKALINE SOLUTIONS*

IX-1. INTRODUCTION

The electrochemical characteristics of CO adsorbed on noble metal surfaces including the nature of the binding sites, and the effects of the applied potential on the structural and electronic properties of the adsorbate/substrate system may be regarded as a mature subject in surface science. Much of the progress in this area is owed to the advent of Fourier Transform Infrared Spectroscopy (FTIR) and more recently Scanning Tunneling Microscopy (STM) as in situ vibrational and topographical probes of the metal/CO(ads) interface, respectively. Extensions of these studies to include more reactive substrates, such as transition metals of the first row, have met with severe experimental difficulties. These are derived primarily from the ease by which the surfaces of these metals oxidize, which render the methods developed for

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the bench-top preparation and handling of noble metals, such as Pt, Rh, and Au,\textsuperscript{3-5} practically inapplicable. Recent efforts in this laboratory have focused on the use of ultrahigh vacuum (UHV)/electrochemical cell transfer strategies for the investigation of CO oxidation on well-defined Ni(111) surfaces.\textsuperscript{6} Based on a combination of temperature programmed desorption (TPD), low energy electron diffraction (LEED) and cyclic voltammetry measurements, it was concluded that a c(4x2)CO layer on Ni(111) protects the underlying surface from undergoing oxidation when placed in an ultra high purity, moist, Ar atmosphere. In addition, this adlayer can be electrochemically oxidized in alkaline solutions to yield well-defined voltammetric features with a total charge corresponding to a coverage of half a monolayer of CO as would be expected for a c(4x2) overlayer.

In a recent report, Castro-Luna and Arvia\textsuperscript{7} concluded on the basis of cyclic voltammetry data that in the case of polycrystalline CO adsorbed on Ni in acid CO is actually desorbed as the (hydrated) nickel hydroxide is formed and \textit{not} electrochemically oxidized.

The results presented in this chapter will show that the voltammetric behavior for CO adsorbed on polycrystalline nickel in 0.1 M KOH solutions bears close resemblance to that reported in acid and neutral media. Furthermore, \textit{in situ} potential difference Fourier Transform Infrared Reflection Absorption Spectroscopy (FTIRRAS) data have provided unambiguous evidence that in this alkaline electrolyte, CO adsorbed on polycrystalline Ni indeed undergoes electrooxidation and \textit{not}
simple desorption (as the underlying substrate is oxidized) to generate solution phase carbonate as the only detectable product.

IX-2. EXPERIMENTAL

In situ FTIRRAS measurements were conducted with an IBM-Bruker IR-98 FTIR spectrometer. A CaF$_2$ dove prism, thin-layer spectroelectrochemical cell similar in design to that described by Seki et al.$^8$ was modified to enable a reference electrode to be placed adjacent to the main cell compartment in a separate chamber sealed from the atmosphere.

The Ni electrode used for these studies was a coin-shaped specimen (Morton Thiokol, Inc. 99.998%) cast in Kel-F exposing a circular cross sectional area of ca. 1.2 cm$^2$ which was polished to a mirror finish with alumina compounds down to 0.05 μm. In order to avoid the unlikely possibility of Pt dissolving in the electrolyte and then plating on the Ni working electrode, a gold wire was used as the counter electrode. The Ag/AgCl electrode was obtained from BAS (W. Lafayette, IN.) and ultra pure KOH from Alfa. No CO adsorption could be detected spectroscopically using lower grade KOH. This is most likely due to the presence of metal impurities, such as iron, that can precipitate on the nickel surface blocking active sites for the adsorption of CO. Research grade carbon monoxide (> 99.99%) was purchased from Matheson. All the experiments were conducted at room temperature.
After the Ni electrode had been polished, it was transferred immediately to the spectroelectrochemical cell. In order to achieve fast potential control (once the working electrode was placed in contact with the electrolyte), the potentiostat was set in the CELL position at a potential of -0.9 V vs. Ag/AgCl with the counter and reference electrodes connected and immersed in the solution. This procedure generates a nominally reduced nickel surface in contact with the solution, and was found to be essential for the success of the experiments herein described. Carbon monoxide was then bubbled into the electrolyte for 5 min. to form the irreversibly adsorbed adlayer and subsequently removed (from the solution phase) by purging with N₂ for 15 min. Prior to the spectroscopic measurements, the electrode was pushed against the optical window with the electrode still polarized at -0.90 V to reduce the thickness of electrolyte in the path of the beam.

IX-3. RESULTS AND DISCUSSION

A. Electrochemistry

The first linear scan in the positive direction initiated at the holding potential of -0.96 V vs. Ag/AgCl for a nominally reduced Ni electrode (see Section IX-2) in 0.1 M KOH is shown in Curve A, Figure IX-1. The anodic peak at -0.64 V has been attributed predominantly to hydroxide ion adsorption with contributions due to surface oxidation to form
Figure IX-1. First linear scan in the positive direction obtained for a nominally reduced Ni electrode prepared in the fashion described in the Experimental Section in 0.1 M KOH before (Curve A) and after (Curve C) saturation exposure to CO (see text for details). Before the scan was initiated the potential was held at -0.96 V vs. Ag/AgCl. Curves B and D are the third voltammetric scans recorded sequentially for the corresponding Ni surfaces in the same potential region. Scan Rate: 0.1 V/s. The dashed lines were used as baselines to determine the charge under the voltammetric peaks.
Ni(OH)$_2$.$^9$

This feature disappears in subsequent scans (see Curve B, Figure IX-1) indicating, as is well known,$^{10}$ that the formation of Ni(OH)$_2$ (from Ni metal) is (electrochemically) highly irreversible. In fact, attempts to reduce electrochemically oxidized surfaces by holding the potential at -1.2 V vs. Ag/AgCl for 10 min. yielded a hydroxide adsorption peak with only a fraction of the charge of that shown in Curve A, Figure IX-1. For this reason (oxidized) nickel electrodes were always repolished before each set of measurements was performed.

Exposure of a freshly polished nickel surface to CO (while holding the potential at -0.96 V) and subsequent removal of solution phase CO by N$_2$ purging, yielded during the first linear scan a peak similar to that observed in the absence of CO, but with the onset shifted about 300 mV in the positive direction (see curve C, Figure IX-1). This behavior is in qualitative agreement with that reported by Castro-Luna and Arvia$^7$ for acid and independently by Hori and Murata for neutral solutions.$^{11}$ As suggested by both research groups, the shift in the onset potential is most likely due to the inhibition of the initial stage of nickel oxidation induced by the adsorbed CO. The charge under the peaks in both curves A and C in Figure IX-1 using the dashed line as a background current was found to be essentially the same (0.87 mC/cm$^2$ and 0.88 mC/cm$^2$ for Curves A and C, respectively). This observation is also in harmony with the reports of Castro-Luna and Arvia$^7$ and Hori and Murata.$^{11}$ It may be noted in this regard that the current following the peak (see Figure IX-1) has a larger
net positive slope for the CO-covered (Curve C) than for the nominally bare surface (Curve A). This is consistent with the ability of adsorbed CO to delay nickel surface oxidation.

B. *In situ* Potential Difference FTIRRAS

To explore the origin of the voltammetric peak on Ni surfaces exposed to CO, the vibrational properties of the interface were examined using *in situ* potential difference FTIRRAS as a probe.

Figure IX-2 shows a series of potential difference FTIRRAS spectra acquired during a slow linear scan in the positive direction at a rate of 0.13 mV/s starting from a potential of -0.90 V vs. Ag/AgCl (see Figure IX-3) using the spectra obtained at -0.76 V, *i.e.* just before the onset of the electrooxidation peak, as a reference. As indicated in panel A, Figure IX-2, the sequence of spectra starting from the onset of the voltammetric peak at -0.68 V exhibits a negative-going peak at around 1890 cm\(^{-1}\), which grows to reach a maximum at -0.43 V which corresponds to the end of the voltammetric feature.

A strong IR band at around 1950 cm\(^{-1}\) has been found for CO adsorbed on evaporated Ni films in ultrahigh vacuum (UHV) and attributed to CO bound to a bridge site.\(^{12}\) This strongly suggests that the feature observed in the *in situ* spectra can also be assigned to the same binding geometry. One possible explanation for the lower frequency observed in the *in situ* data may be found in the work of Weaver and
Figure IX-2. Series of potential difference FTIRRAS spectra in the regions between 1790 and 1970 cm\(^{-1}\) (Panel A) and 1280 and 1530 cm\(^{-1}\) (Panel B) acquired during the slow scan in Figure IX-3 using the spectra obtained at -0.76 V, i.e. before the onset of the electrooxidation peak, as a reference. All potentials are given vs. Ag/AgCl.
Figure IX-3. First linear scan recorded during the FTIRRAS spectral measurements at a rate of 0.13 mV/s. Otherwise, all conditions are the same as those in Caption Figure IX-1.
co-workers,\textsuperscript{1,13} who reported that in the case of the low index faces of single crystal Pt, the stretching frequencies of adsorbed CO for a given adsorption site, are always 30-50 cm\textsuperscript{-1} larger in UHV than in electrochemical environments. This effect has been ascribed to the less positive potentials (lower work functions) that can be achieved in electrochemical compared to UHV environments.\textsuperscript{1}

It must be stressed that the results shown in panel A, Figure IX-2 simply prove that as the potential is made positive adsorbed CO disappears from the surface, either by (intact) desorption, as proposed by Castro-Luna and Arvia\textsuperscript{7} in acid media or by electrooxidation as suggested by Hori and Murata\textsuperscript{11} for neutral electrolytes. Unambiguous evidence in support of the latter possibility is provided by the in situ FTIRRAS results shown in panel B, Figure IX-2. In particular,

(i) The spectra show a positive-going band at about 1400 cm\textsuperscript{-1} attributed to solution phase carbonate derived from the two-electron electrooxidation of adsorbed CO.

(ii) The potentials at which this band first emerges and later reaches maximum intensity coincide with those corresponding to the onset and to the end of the voltammetric feature (see Figure IX-3), respectively.

Also noteworthy is the frequency shift of the bridge-bonded CO band as the oxidation of CO proceeds. This can be more clearly seen by choosing the spectrum taken at -0.39 V vs. Ag/AgCl i.e., after the end of the peak, as a reference (see Figure IX-4), a potential for which the
Figure IX-4. Series of (smoothed) potential difference FTIR-RAS spectra in the regions between 1780 and 1950 cm\(^{-1}\) using the spectrum obtained at -0.39 V, i.e. after the electrooxidation peak, as a reference.
coverage of CO becomes essentially zero.

Unfortunately, it is not possible to determine the actual coverage of CO on the Ni surface, mainly because the peak centered at -0.64 V (see Curve C, Figure IX-1) may contain in addition to the electrooxidation of adsorbed CO, contributions due to surface processes associated with the electrochemistry intrinsic to the underlying substrate (see above).

Some indication of the relative coverages of CO as a function of potential can be obtained using the area of the solution-phase carbonate band observed at the most positive potential as a normalization factor (see Panel B, Figure IX-2). This procedure appears more accurate than that based on the adsorbed CO-band since the absorption cross section for bridge-bonded CO on Ni has been reported to vary as a function of coverage.$^{12,14}$ These data can be combined with those in Figure IX-4, to construct a plot of $ν_{CO}$ vs. the normalized CO coverage (see Figure IX-5). As clearly seen, $ν_{CO}$ increases linearly with the normalized coverage. A qualitatively similar behavior has been reported for bridge-bonded CO on Ni(111) in UHV studies by Surnev et al,$^{14}$ and also for bridge-bonded CO on Pt single crystal surfaces in aqueous electrolytes.$^{15}$ Unlike the results obtained for Pt,$^{16}$ however, no changes in the magnitude of $ν_{CO}$ could be detected as a function of potential in a range negative to that required to oxidize CO.
Figure IX-5. Plot of $\nu_{\text{CO}}$ (from Figure IX-4) vs. the normalized CO coverage determined from the data in Panel B, Figure IX-2 (see text for details).
IX-4. SUMMARY

Based on the electrochemical and in situ FTIRRAS data presented in this study for the Ni(poly)/CO(ads) system in 0.1 M KOH it may be concluded that:

(i) Carbon monoxide adsorbed on Ni(poly) shifts the onset of surface oxidation by about 300 mV toward more positive potentials compared to the nominally bare substrate. In addition, the areas under the prominent peak obtained in the first scan in the positive direction for both bare and CO covered surfaces are essentially identical. These observations are in agreement with those reported by other workers in acid and neutral electrolytes and suggest that the voltammetric features in the whole pH range are associated with the same surface processes.

(ii) The in situ FTIRRAS results have indicated that the potentials associated with the onset (and the end) of the voltammetric peak coincide with the emergence (and limiting intensity) of the spectral feature attributed to solution phase carbonate. This provides unambiguous evidence that the prominent peak observed in the first linear scan may be (largely) ascribed to the electrooxidation of adsorbed CO. This is in accordance with the suggestions put forward by Hori and Murata\textsuperscript{11} in neutral media, but at variance with the views of Castro-Luna and Arvia\textsuperscript{7} who proposed that CO (in acid electrolytes) undergoes a simple desorption as the surface is oxidized.

(iii) No changes of $v_{CO}$ could be detected as a function of potential
in a range negative to that required to oxidize the species. In analogy with
the behavior reported for CO adsorbed on Ni(111) in UHV and that for Pt
in aqueous electrolytes, however, $v_{\text{CO}}$ was found to shift toward lower
wavenumbers as the coverage of CO reduced by electrooxidative
stripping.

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CHAPTER II


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CHAPTER VI


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CHAPTER VII


CHAPTER VIII


CHAPTER IX


